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AMERICAN LEATHER CHEMISTS ASSOCIATION

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IMPORT - EXPORT

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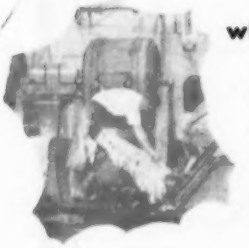
Our technically trained leather chemicals salesmen working in the field have the complete backing of a highly specialized leather research staff working in the Rohm & Haas Leather Laboratories. For years, these specialists in leather chemistry have been engaged in a study of leather, its uses and its many process problems. The knowledge and experience gained over the years from this research are available to you through your Rohm & Haas salesman.



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Process problems that cannot be handled in the field are brought to our experimental tannery for detailed study and analysis. Here we have simulated a commercial leather-making operation, a tannery-in-miniature which provides small-scale facilities for running tests on many kinds of leather. Problems are handled in a thorough, practical way.

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OROTAN—synthetic tanning material providing in itself a complete replacement for natural tannings.

PRIMAL—leather finishing materials in the form of aqueous dispersions of acrylic resins.

Whatever your leather problems may be, it will pay you to talk them over with your Rohm & Haas representative.

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NON-TANNIN . . .	16.03	17.14
INSOLUBLES . . .	1.70	0.72
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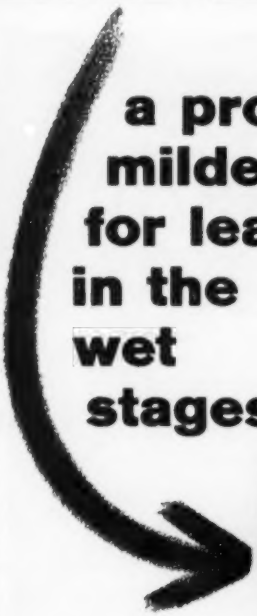

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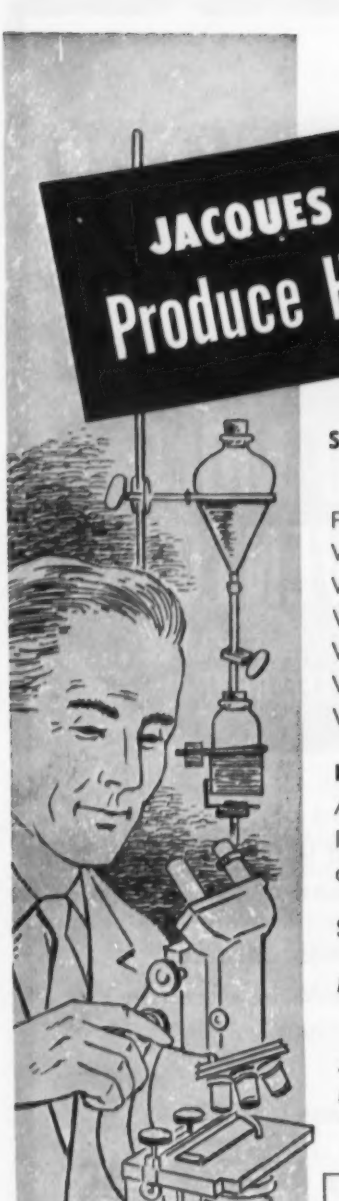

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FAT LIQUOR 0-270

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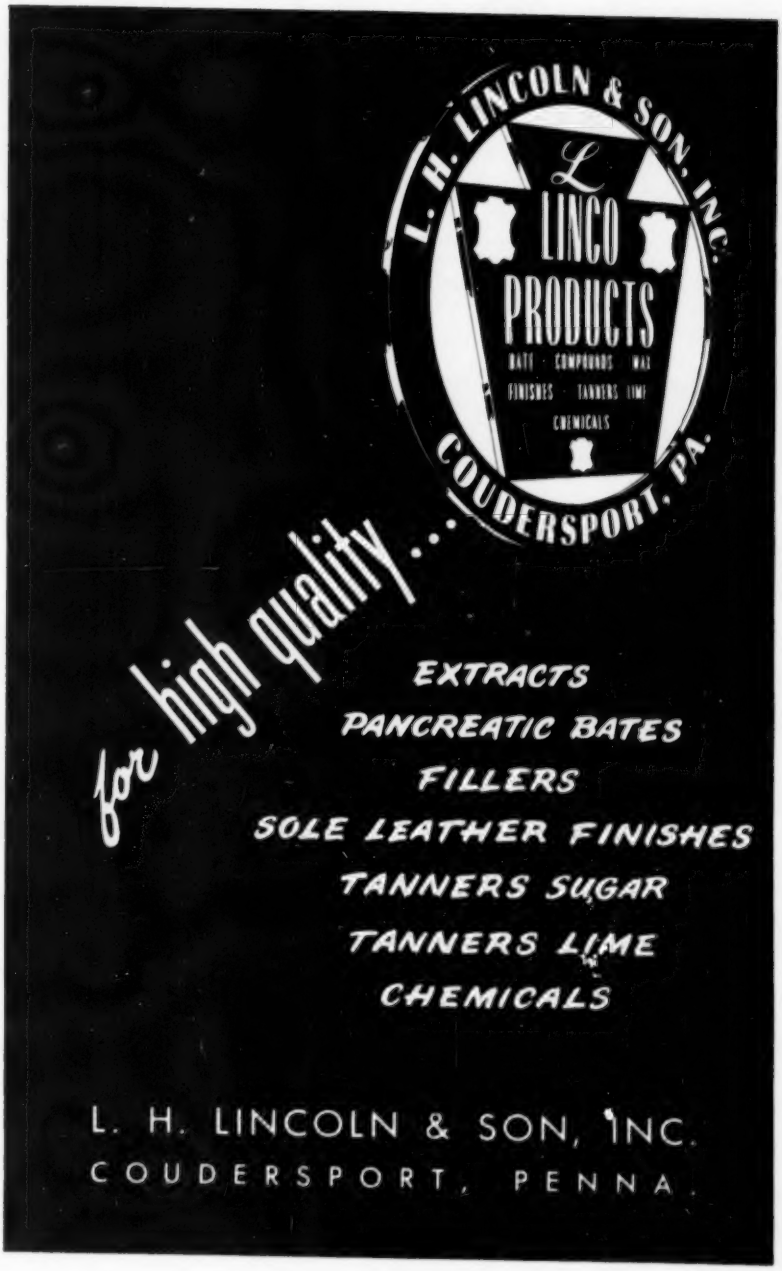
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CHEMICALS
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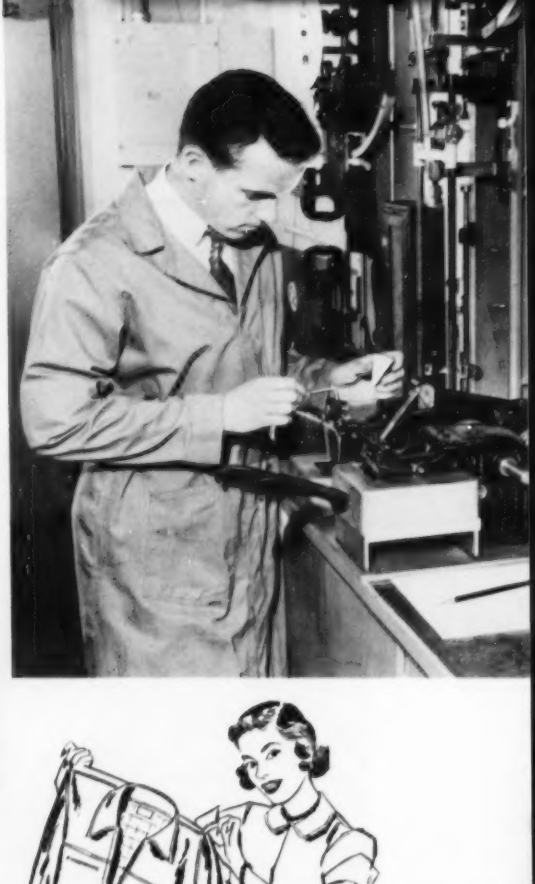
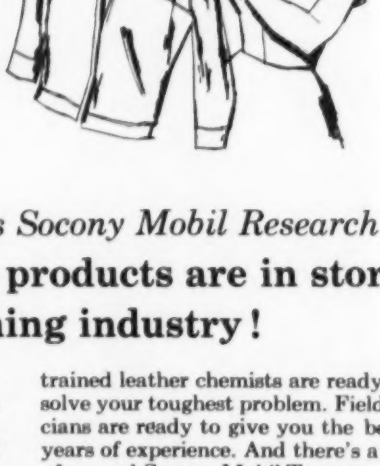
Improved waterproofing compounds for upper leathers are being developed and tested by Socony Mobil scientists. The goal is upper leathers with a new degree of water resistance.



Tanners products to make suedes water-repellent and dry-cleanable—long an aim of the leather industry—are now in the development stage at Socony Mobil's leather products laboratory.



Thanks to Continuous Socony Mobil Research

New and improved products are in store for the tanning industry!

Socony Mobil leather chemists are constantly at work *for you!* Two of their most significant projects are shown above. Water-repellent, dry-cleanable suedes and improved water-proofing compounds for upper leathers.

This constant search for new methods and new products is just one of the many ways Socony Mobil serves the leather industry. Extensive laboratory facilities and trained leather chemists are ready to help solve your toughest problem. Field technicians are ready to give you the benefit of years of experience. And there's a full line of proved Socony Mobil Tanners products to meet your every need.

* * *

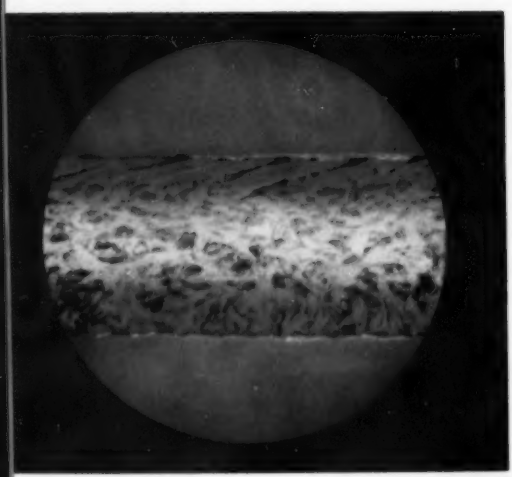
You can rely on Socony Mobil Research—to speed progress . . . increase profits for the tanning industry!

Socony Mobil Tanners Products

SOCONY MOBIL ANNOUNCES

Mobiltan 275

Specifically developed for fat-liquoring of pasted-side upper leather!



Cross-section photomicrograph illustrates controlled penetration of Mobiltan 275. Special qualities permit surface nourishment and enough penetration to give the desired mellowness.

Mobiltan 275 is a carefully compounded, relatively complete fat-liquor that will give excellent results in both full and corrected grains of pasted-side upper leather. Years of research and exhaustive field testing have resulted in a compound with these desirable properties:

- Non-oxidizing and light fast
- Controlled penetration for balanced lubrication
- Forms a stable emulsion at normal operating temperatures
- Exhausts readily with normal running time
- Compatible with resin re-tannages
- Low moisture content

For more information on how Mobiltan 275 can improve your production and cut your operating costs, contact your Socony Mobil representative.

Mobiltan 275 in solution shows an alkaline pH reading — truly an alkaline fat-liquor.

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First choice with Tanners since 1866

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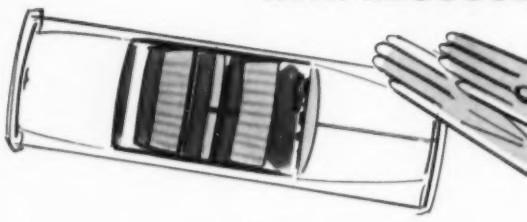

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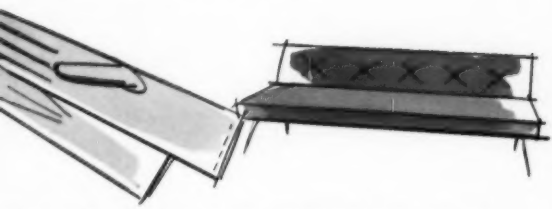

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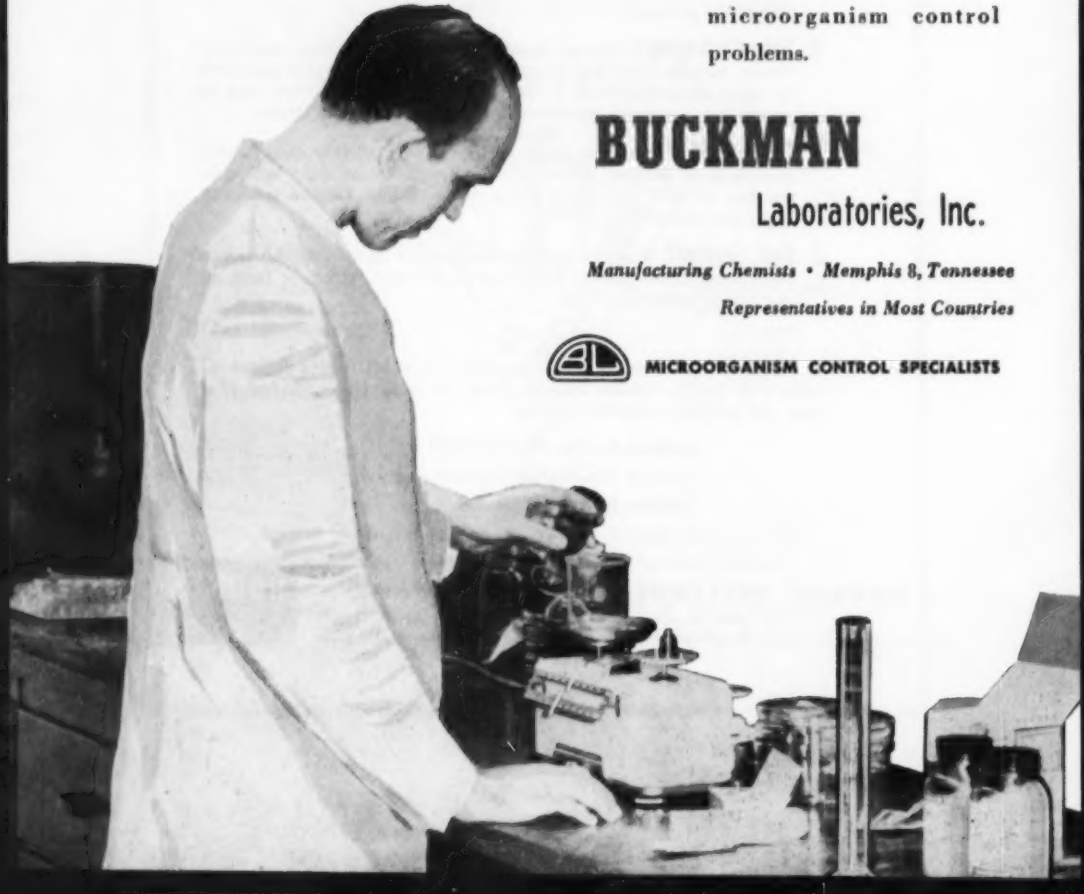

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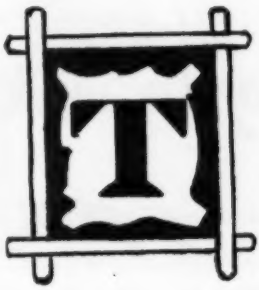

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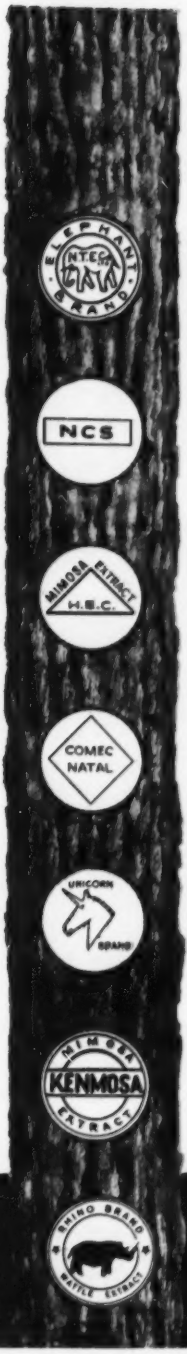

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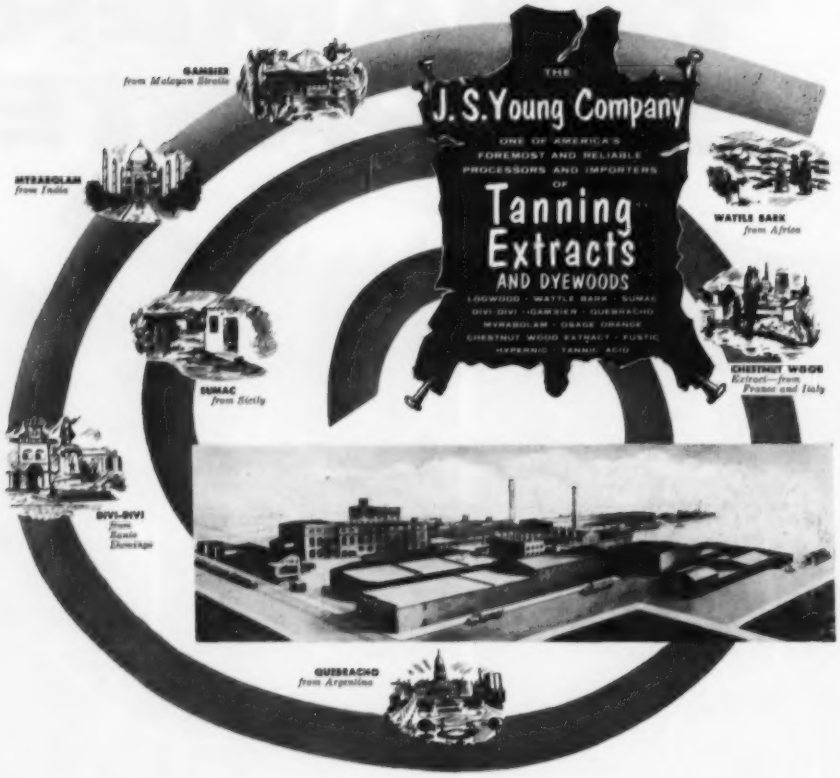
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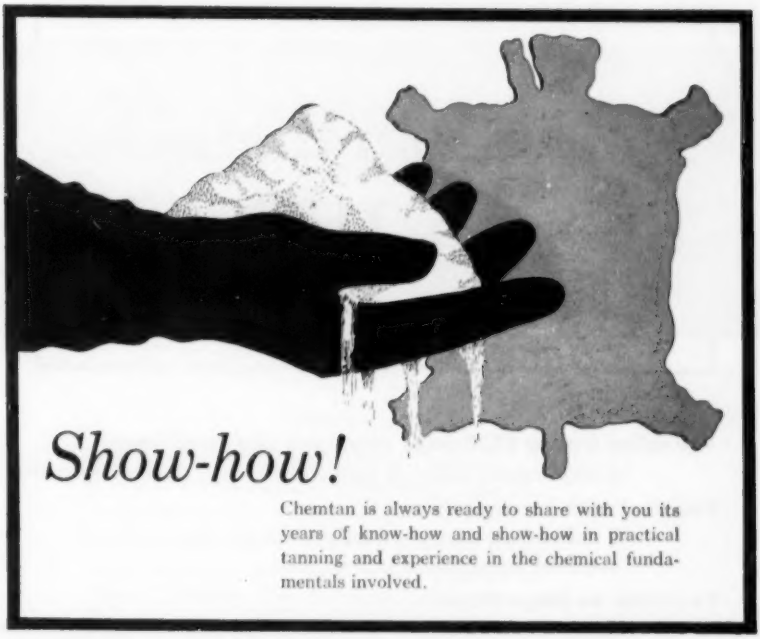
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PRACTICAL CONSIDERATIONS IN WATERPROOFING LEATHER

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ABSTRACT

A new type of tester for measuring resistance to water penetration has been developed. This instrument measures the time required for water penetration when the leather is subjected to intermittent pressure in contact with a wet surface. Results obtained with this machine on glove leathers show better correlation with practical tests than results obtained with flexing machines.

INTRODUCTION

Of the many recent developments that are currently under investigation in the leather industry, perhaps the one receiving the greatest attention is that of improving water resistance characteristics. Although processes and treatments designed to improve these characteristics of leather date back several decades or longer, significant improvements over older methods have been made within the last few years.

A very interesting report by Maeser (1) made a significant contribution to our understanding of the problem of waterproofing leather by demonstrating the necessity for dynamic methods of testing. This technique simulates the conditions that are met in the wearing of a leather shoe in mud or water. The older static test methods were shown to be unreliable as the results did not correlate with those obtained in shoe-wearing trials.

The dynamic water penetration apparatus and test method developed by Maeser have been adopted in many laboratories and applied to shoe upper leather, for which the test was designed. The application has been extended also to many other types.

The development of water-resistance leather has been the subject of a great deal of study by the Quartermaster because of the urgent need of providing greater protection for the hands and feet of the soldier under extreme weather conditions. The problem is particularly acute, and may become critical, under wet cold conditions. This paper will describe several experiments in the evaluation of leathers treated for water resistance in the laboratory, as well as glove-wearing trials under simulated field conditions. It will also describe a new method of measuring water resistance of leather under dynamic conditions.

*Presented at the Fifty-second Annual Meeting, Mackinac Island, Michigan, June 19, 1956.

PRELIMINARY EXPERIMENTS WITH WATER-RESISTANT GLOVE LEATHER

In a Quartermaster project on the development of water-resistant glove leather, several laboratory test methods were used in the preliminary evaluation of the experimentally treated leathers, after which the more effective treatments were selected for futher trials and field tests. In these experiments the dynamic Maeser test proved superior to the static methods for screening purposes, although none of the tests was entirely satisfactory for predicting serviceability under field conditions. A comparison of the results is shown in Table I.

TABLE I

RESISTANCE OF 2.5-OUNCE HORSEHIDE GLOVE LEATHER TO PENETRATION BY WATER IN LABORATORY AND FIELD WEAR TESTS

	MAESER TEST			GLOVE-WEARING TRIALS	
	Cycles to First Leak Run No.*			Minutes to First Leak	
Type of Leather	1	2	3	Stacking Wet Bricks	Working on Rain Course
POLYACRYLATE–TREATED					
Hide No. 1	10,000+	10,000+	10,000+		
Hide No. 2	10,000+	2,300	10,000+	6.5	12.5
Hide No. 3	10,000+	10,000+	9,400+		
UNTREATED	375			1.5	9.6

*Successive runs on same specimen, dried between runs.
+Plus sign indicates that specimen did not leak.

The results of the laboratory tests showed the low resistance of untreated leather and indicated a high degree of water resistance for the treated leathers. Three trials were made on each of the treated hides with thorough drying at room temperature between runs. In seven of the nine tests the leather resisted water penetration for more than 10,000 cycles, or approximately two hours. The glove-wearing trials were of two types: in one, soldiers lifted and moved wet objects on a glove course under controlled simulated rainfall; in the other (wet brick test), a leather technologist turned, lifted, and stacked bricks from a resting position in approximately one inch of water. The gloves worn in the wet brick test had the seams sealed to prevent leakage whereas those worn in the field were unprotected. A small amount of seam leakage may account for the smaller difference between treated and untreated leather observed on the glove course. The faster penetration noted in the laboratory may have been due to a difference in the degree of wetness at which the wearer felt sure of a wet feeling. In both cases, however, it is readily apparent that the difference in water resistance of treated and untreated leather is far less than that indicated by the laboratory tests.

Other phases of the glove-wearing trials included measurements of drying time, the feel of the leather, and performance characteristics that must be considered in evaluating the effectiveness of the treatment in improving the properties of glove leather. The over-all evaluation demonstrated a very significant improvement despite the failure to attain a high degree of resistance to water penetration. Although the other characteristics are considered important and closely related to water resistance properties, they are beyond the scope of this report.

In a second experiment, deerskin leather for Arctic mitten shells was treated for water resistance by two processes, namely: polyacrylate impregnation and a silicone process. Maeser penetration values for the treated leathers ranged from approximately 8,000 flexes to 40,000 flexes without penetration, thus indicating very effective treatments. The water-resistant leathers were manufactured into mitten shells for wear on the glove course in handling wet objects. The results, like those in the previous test, proved that the treated leathers were only slightly more resistant to water penetration than similar untreated deerskin leather.

These experiments on horsehide and deerskin leather demonstrated the need for an improved screening technique, as the laboratory tests failed to provide a true indication of the water reistance properties of glove leather. In searching for an explanation of these findings it became apparent that glove leather offers little resistance to the flexing action of the Maeser test because of its softness and flexibility. Consequently, the flexing fails to apply stress to the specimen as in the case of the thicker and stiffer shoe upper leathers for which the method was designed.

The stresses and strains in the creases which apparently force water through a specimen in the flexing process are largely dependent on other physical characteristics, such as stiffness, elongation, compressibility, and thickness. For example, a report by Wier *et al.*(2) demonstrated the effect of thickness on the time required for water penetration of side upper leather. Very thin layers were penetrated only after a tremendous number of flexes despite the relatively poor performance of the unsplit leather. Therefore, it is not surprising to find that the mere bending of a relatively thin, soft specimen of water-resistant leather fails to produce the dynamic force required for water penetration. Mild flexing action such as this does not correspond to the more severe conditions that are generally met in normal wear of a work glove. For example, the leather in the palm area is repeatedly squeezed between the hand and the object being handled. This cyclic process, applying and releasing pressure, results in a pumping action that forces the entrapped air out of, and water into, the spaces between the leather fibers. If the fibers are not effectively treated, the pumping action will generally proceed until water penetrates the leather or until it is completely saturated. Specially treated leather fibers may effectively resist the pumping action, the length

of time depending upon the stress applied. There are indications of the existence of a critical stress for any particular specimen that is just sufficient to overcome the resistance to penetration by water within a small number of cycles. If a lower stress is applied, less than the critical value, a very large number of cycles may fail to cause penetration.

With this mechanism of the water penetration process in mind, it appeared that a dynamic straining technique similar to that applied to the palm of a glove might be devised to provide a suitable method for measuring water resistance of soft types of leather. Preliminary trials were made with a modified Maeser test. Two steel balls, 1″ and 7/8″ in diameter, were placed in the specimen trough so as to squeeze the leather in the crease between them with each flexing stroke. This modification proved effective in reducing the time required for water penetration of treated horsehide glove leather from approximately ten thousand to a few hundred flexes. Although this technique showed promise, it was discontinued because it did not provide a convenient means for adjusting the critical spacing between the balls for differences in specimen thickness.

Several attempts were made to devise a cycling mechanism to apply a uniform stress to a specimen, using flexing, tension, and pressure techniques. The pressure method proved to be most satisfactory in minimizing the effects of variations in thickness and stress-strain characteristics. A dynamic method was developed which provided a convenient means for applying uniform stress to a specimen while in contact with a wet surface.

TAPPING TEST APPARATUS

The apparatus, shown in Figure 1, consists essentially of the following parts:

1. A rotating anvil which provides a uniform wet surface,
2. An arm and hammer to provide a definite force per unit area on the specimen, and
3. A cam mechanism for lifting and releasing the hammer, thus allowing it to fall on the anvil.

The specimen is mounted on the end of the arm with the flesh or unexposed side in contact with the hammer. In each cycle or stroke the fall of the hammer causes the specimen to strike the wet anvil, thus applying the necessary force to strain the fibers. The specimen rubs against the rotating wet anvil under pressure until the cam lifts the arm. The tapping and rubbing action is repeated with each cycle. Penetration of the leather by water completes an electrical circuit through the arm and the rotating anvil to sound a buzzer, thus providing a well defined end point of the test. The load applied to the hammer is ½ lb. and the hammer falls a distance of ½″ in tests of glove leather.

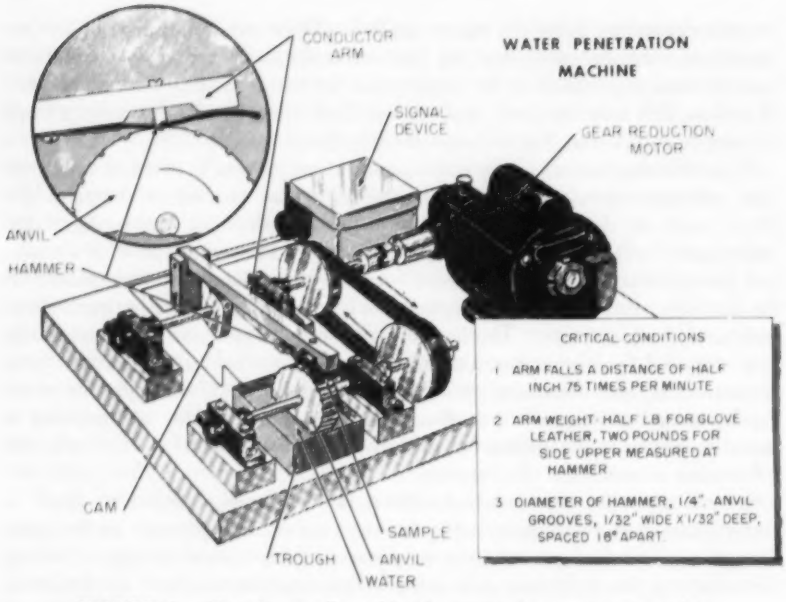
CONDUCTOR ARM
WATER PENETRATION MACHINE
SIGNAL DEVICE
GEAR REDUCTION MOTOR
ANVIL
HAMMER
CRITICAL CONDITIONS
1 ARM FALLS A DISTANCE OF HALF INCH 75 TIMES PER MINUTE
2 ARM WEIGHT HALF LB FOR GLOVE LEATHER, TWO POUNDS FOR SIDE UPPER MEASURED AT HAMMER
3 DIAMETER OF HAMMER, 1/4". ANVIL GROOVES, 1/32" WIDE X 1/32" DEEP, SPACED 18° APART.
CAM
SAMPLE
TROUGH
ANVIL
WATER

FIGURE 1.—"Tapping test" machine for measuring water penetration.

The results of tests on glove leather are shown in Table II.

It may be observed that water penetrated untreated leather in twenty cycles or less in the tapping test. The treated leathers varied in their ability to resist penetration, ranging from 15 to 70 cycles. The Maeser values are below 500 cyles for untreated leather and above 9000 cycles for the two treated leathers tested. It is apparent that the latter results are very different from those in the tapping test, especially for the treated leathers. The ratios of the paired values range from 8 to more than 432. The treated horsehide No. 1 is the same as that reported in Table I, which first leaked in the wet brick test in 6.5 minutes. A similar test of a glove made of treated cowhide No. 3 showed the first leak in 12 minutes. The results of the glove-wearing trials are in satisfactory agreement with the results of the tapping tests.

Penetration of both treated and untreated leather was faster than expected in the tapping test; therefore, adjustments were made to reduce the stress applied to the specimen and the speed of penetration. It was thought that this modification might improve the method by increasing the range of the test values and produce wider differences among treated leathers. An experiment was made to determine the effect of a change in the pressure applied to the specimen on the penetration time. The pressure was varied by adjusting the weight at the center of the hammer in several steps from 4 to 40 ounces.

TABLE II

WATER PENETRATION OF GLOVE LEATHERS
COMPARISON OF TAPPING AND MAESER TESTS

Type of Leather	No. of Trials	CYCLES TO FIRST LEAK		Ratio Maeser/ Tapping
		Tapping* Average	Maeser Average	
UNTREATED				
Horsehide	6	10	375	38
Cowhide	4	20	155	8
Deerskin	6	8	490	6
Sheepskin	4	17	490	29
TREATED				
1. Horsehide, polyacrylate	8	21	9080+	432+
2. Horsehide polyacrylate	6	70	—	—
3. Cowhide, Quilon‡ and polyacrylate	3	68	10,000+	147+
4. Horsehide, silicone	3	15	—	—
5. Cowhide, silicone	2	28	—	—

*Using ½-lb. load and hammer falling ½ inch.
+Plus sign indicates one or more specimens did not leak.
‡A proprietary compound said to be stearato chromic chloride.

The distance through which the hammer was allowed to fall was also varied in order to study the effect of the impact on the rate of penetration. The results of these tests are presented in Figure 2.

The results show that the number of cycles required for penetration decreases with either an increase in load or an increase in the height of fall of the hammer. It is apparent from the slopes of the curves that the effect of load is relatively small within the range covered and that the height of fall has a much greater effect. Although a fall of less than ½″ resulted in a larger number of cycles for penetration, this advantage appeared to be outweighed by the possible need of an adjustment for specimen thickness under such conditions. Therefore, in order to standardize the procedure, a height of ½″ and a load of ½ lb. were selected for use in routine tests of glove leather.

MEASUREMENT OF WATER RESISTANCE—GENERAL CONSIDERATIONS

Thus far, only one measure of water resistance has been considered, namely, the time required for first penetration. There are several other measurements

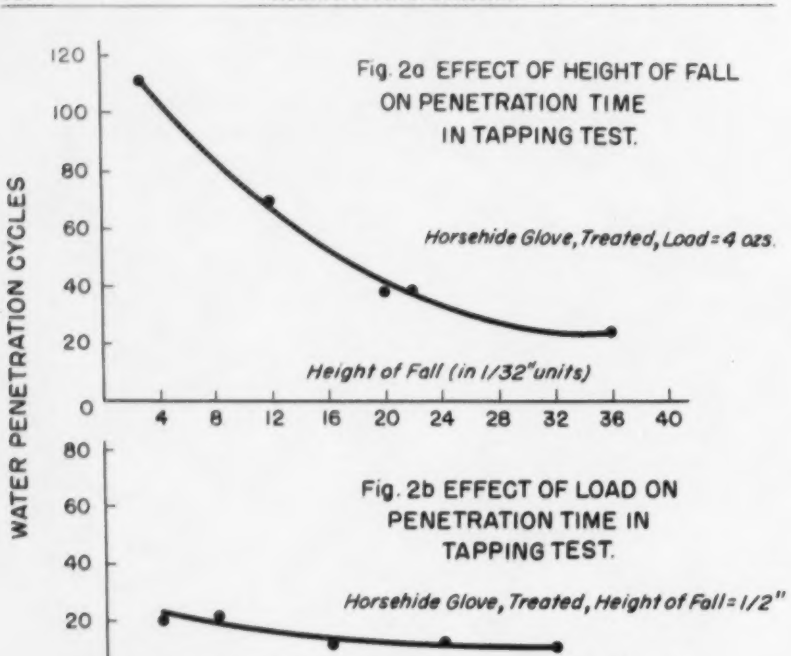

FIGURE 2.—Relation between (*a*) height of fall and (*b*) load on time required for water penetration.

that might be considered equally important under certain conditions, such as the rate of water penetration, the amount of water absorbed by the specimen, and the effect of water on the surface finish. All these properties were considered, as they could have been measured by slight modifications of the tapping test. The selection of the time of first penetration as an indicator of water resistance was made because it appeared to be more closely related than other properties to the characteristics desired in military leather for handwear and footwear. The goal of this development project is an effective process of preventing water penetration, thereby maintaining the insulating qualities of gloves and boots as well as the glove inserts and socks. Resistance to penetration is considered essential because the lining materials provide effective insulation only as long as they are kept dry.

The rate of water penetration has been proposed as a measure of water resistance. This property is perhaps more applicable to water-repellent than to highly

water-resistant leathers, as it is measurable only if water penetration cannot be prevented. Data will be presented below to show that several commercial processes are capable of producing both glove and upper leathers that do not leak before the test time becomes excessive. If penetration does occur, the rate of penetration does affect the wetness of a glove insert. However, there are indications that the rate of penetration may have less effect on comfort than the initial penetration point. For example, in wearing cross-mated gloves, treated and untreated under wet cold conditions, greater differences in comfort generally are felt after only one glove leaks than after both gloves leak.

The insulating qualities and comfort of leather are also related to the amount of water absorbed by the leather. After the initial wetting of the leather surface, the amount of absportion generally increases at a steady rate with no abrupt change when the entire thickness is penetrated. Therefore, absorption is not closely related to the sudden change to a cold or wet feeling with the initial water penetration. Water absorption also is dependent upon grease content which, within the usual range up to approximately 30%, has little effect upon resistance to water penetration. An additional objection to the use of low water absorption as an optimum water resistance property is the fact that it conflicts with the high perspiration absorption property desired for maximum comfort in leather for shoes, gloves, and garments.

The degree of water resistance discussed above is only one of many different degrees of water repellency currently under development in the leather field. Various terms are in common usage to describe these water-resistant leathers, such as "waterproof", "water-resistant", "water-repellent", and "shower-proof". However, these terms are too indefinite to provide precise descriptions of water resistance characteristics. Although a clear-cut definition of water resistance and a standard method of evaluating all types of leather might be developed, the problem would remain, as there are many different degrees of water resistance required in various applications. For example, a water-repellent treatment which prevents wetting of the outer surface of leather exposed to a slight shower serves a very useful purpose, despite the fact that the leather may leak quickly under moderate stress. The degree of water resistance required in this case is much less than that of the palm of a glove. Therefore, a treating process might prove satisfactory for garment leather but entirely unsatisfactory for glove leather. Experimental evidence to this effect has been obtained in a few trials of garment leather treated by several commercially acceptable processes. This leather showed only slight improvement over untreated leather in the tapping test, although service tests showed it to be satisfactory. Applications of the same processes to glove leathers also have been unsuccessful in improving resistance to water penetration.

Increasing the water repellency of the leather fibers is sometimes said to be the goal of certain waterproofing processes. There is little doubt that this

goal can be attained by several methods with satisfactory results for the purpose intended. Here again the result can be easily misinterpreted, as numerous examples, such as those reported by Weir *et al.* (2), show that treatments that are effective in increasing water repellency of the fibers of side upper leather often reduce the capacity of leather to absorb and hold water, thus causing the leather to be penetrated more quickly under dynamic conditions than untreated leather.

APPLICATION OF THE TAPPING TEST TO SHOE LEATHER

The upper leather of a military or work shoe is subjected to considerable stress, not only in flexing but also in twisting and bumping against hard objects. Therefore, a relatively high degree of water resistance is required to prevent leakage under wet conditions. Experience with the Maeser test has confirmed the results of field trials in demonstrating that water will penetrate untreated leather within a few minutes and that a very substantial improvement is possible by several different commercial processes. In order to extend the comparison of the tapping test with the Maeser test to side upper leather, experiments were made on a group of treated and untreated specimens. Preliminary trials of the tapping test showed that a load of 2 lb. on the hammer falling from a hight of ½″ provides adequate stress for side leather. Typical results are presented in Table III.

TABLE III

EFFECTS OF TREATMENT ON WATER PENETRATION OF SIDE UPPER LEATHER

Type of Leather	No. of Trials	CYCLES TO FIRST LEAK	
		Tapping* Average	Maeser Average
UNTREATED			
Chrome, fatliquored	10	52	137
Retan, stuffed	6	144	113
TREATED			
1. Chrome, silicone	8	930	550
2. Chrome, silicone	1	106	7500+
3. Chrome, silicone	1	56	195
4. Chrome, silicone	3	1059	9900
5. Retan, Bavon‡	4	2650	15,000+
6. Chrome, Bavon	1	505	—
7. Chrome, Bavon	2	712	—
8. Chrome, Bavon	6	4500+	66,000+
9. Retan, Hopton process	3	3500+	6,770+

*Using 2-lb. load and hammer falling ½ inch.
+Plus sign indicates one or more specimens did not leak.
‡A proprietary compound said to consist of water-insoluble alkylated succinic acids. See U. S. Patent 2,643,996, Nov. 9, 1954.

It may be observed that the fatliquored chrome-tanned leather was penetrated more quickly in the tapping test than the stuffed retan leather. This difference is considered to be of no practical significance, however, as both types leak very quickly in this, as well as the Maeser test. The effects of the treatments are much more significant. With only one exception, the treated leathers show considerable improvement over the untreated leathers. Treatment No. 3 apparently was ineffective, but the remaining treatments vary in their effectiveness up to very high values. The highest result obtained in the tapping test on this group was 4500 cycles or one hour, at which time the test was discontinued without penetration. A previous Maeser test on this lot of leather had run for 66,000 flexes without penetration. Treated leather No. 9 was tested in three locations on a side; two showed no penetration, but the third was quickly penetrated in both the tapping and Maeser tests. These results indicate incomplete or irregular coverage, which is to be expected in the early trails of any process. Although it is apparent that either high or low values on the tapping test generally are associated with correspondingly high or low values on the Maeser test, there are exceptions. For instance, treated leather No. 2 showed low resistance to penetration on the tapping test, but 7500 flexes without penetration on the Maeser test. Differences such as this have been observed in several other instances, particularly in the case of silicone-treated leathers. However, every specimen requiring more than 2000 cycles in the tapping test also has required a large number of cycles in the Maeser test.

As in the case of glove leather reported in Table II, water penetration of cowhide upper leather is faster in the tapping test than in the Maeser test. Although the difference is small for untreated leathers, it increases rapidly with the more effective treatments. The greater speed of penetration in the tapping test is an advantage. It is generally possible to determine whether or not a specimen shows promise in resisting water penetration in approximately ten minutes or 750 cycles in the tapping test compared with an hour or longer in the Maeser test.

The water resistance treatments reported in Table III showed substantial differences in their effectiveness. This raised a question regarding what might be expected of their performance in boots worn under wet conditions. In an attempt to answer this question two pairs of water-resistant treated leather boots were obtained for preliminary wading trials. It was thought that these experiments might furnish information regarding the degree of water resistance necessary in upper leather to provide significant improvements in the water resistance of a boot. The upper leather of one pair of boots was treated by a silicone process and the other pair by a Bavon* process, the treatments being the same as Nos. 4 and 5 respectively reported in Table III. The first wading trials were unsuccessful because of quick seam leakage despite the

*See footnote, Table III.

fact that both pairs were specially constructed to prevent this type of leakage. The inseam and welt-upper juncture proved to be the areas leaking most and also the most difficult to seal. However, after the seam leakage was stopped the wading trials showed the first leak through the silicone-treated upper leather in 60 minutes compared with 270 minutes for the Bavon-treated leather. These results are in satisfactory agreement with the relative values obtained in the tapping tests on treatments Nos. 4 and 5 of Table III. The superiority of treatment No. 5 is also evident in the Maeser test, but the extent is indefinite as the test was discontinued at 15,000 cycles without a leak.

APPLICATION TO COWHIDE GLOVE LEATHERS

Further application has been made of the tapping test in the development of a more effective water-resistant process for cowhide glove leather. This screening technique has shown several advantages over previous methods. One in particular is the speed of the test, as only a few of the most effectively treated leathers require more than a few minutes for penetration. A convenient feature is the ease with which a glove can be fastened over the end of the arm for testing purposes. Another important advantage is the small test area used. This allows a specimen to be tested and then processed further in a series of trials until the desired result is obtained. A few examples illustrating the degree of water resistance attained in recent trials are shown in Table IV.

TABLE IV

EFFECT OF TREATMENT ON WATER PENETRATION OF COWHIDE GLOVE LEATHER

Treatment	% Applied	Tapping Test* (cycles) ½ lb. Load	Tapping Test* (cycles) 2-lb. Load
Bavon†	8	2250+	2100
Bavon and Quilon**	8	2250+	1400
Thiokol	25	2250+	380
Thiokol and silicone	27	2250+	800

*Each value is the average of three or more trials.
† See footnote, Table III.
+ Plus sign indicates that specimens did not leak in 30-minute test.
**See footnote, Table II.

The results show that all the treated cowhide glove leathers resist leakage for more than 2250 cycles in the usual ½ lb. glove test. This compares with the maximum value of only 70 cycles for treated glove leather reported in Table II. Further trials were made on the same specimens using the 2-lb. load

generally applied to shoe upper leathers, the heavier load being used here in order to reduce the time of the test. The results demonstrated that a high degree of water resistance is possible with 2.5-oz. glove leather. In fact, the results compare very favorably with the results on treated side upper leather presented in Table III.

SUMMARY

Screening tests with the Maeser apparatus proved unsatisfactory for predicting the performance in wear under wet conditions of leather gloves treated for water resistance. The flexing of a soft specimen of water-resistant leather does not produce the dynamic stress and strain necessary to pump water through the leather. The Maeser flexing test which was designed for shoe upper leather is not applicable to soft, flexible types of leather.

A new machine for testing glove leather, as well as shoe upper leather is described. The new dynamic test employs a tapping and rubbing action to apply stress to a specimen in contact with a wet surface. The tapping test causes faster penetration than the Maeser test, especially on the more resistant types of leather. The results of a few glove- and shoe-wearing trials have shown satisfactory agreement with the results of the tapping test.

The water-resistant characteristics of leather for different applications are discussed. Particular emphasis is given to the high degree of resistance to water penetration required in military leather for gloves and boots and the promise shown by several new processes of meeting the requirements.

ACKNOWLEDGMENT

The author appreciates the assistance of Mr. C. P. Merhib in designing and constructing the prototype of the new tapping test apparatus and in conducting many of the tests. Mr. E. C. Dogliotti also contributed very helpful suggestions in the development of the apparatus and conducted some of the tests.

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2. Weir, C. E., J. Carter, S. B. Newman, and J. R. Kanagy. *JALCA*, **43**, 69 (1948).

Received September 4, 1956.

DISCUSSION

MR. N. C. BENRUD (S. B. Foot Tanning Company): I want to thank Dr. Mann for taking the initiative to present this paper. It is about a new and controversial development, and we hope it is a forerunner of many papers dealing with this subject.

I think advertising has created the impression that we are making a waterproof leather, but all tanners who have worked with these new materials know that we are imparting water repellency features and not waterproofness. To make leather waterproof we must fill all voids in the fiber structure and make the barrier, so formed, flexible and permanent. To do so would destroy the porosity and breathing characteristics of leather. We would have made a substitute for a rubber boot. Instead, we have, with the help of these new products, produced a series of leathers with new and improved properties. We must test and study these features in order to make the best use of them and to get the greatest value from them.

The public must be correctly informed of their value. This requires testing devices. Dr. Mann found that existing testing devices did not correlate with working conditions for glove leathers. A compression factor on the grain side was needed. This has been built into his test machine.

MR. C. ALLEN LAUDER (Wickett & Craig, Ltd.): When you were working with these wet bricks, did you make any tests at all on the wearing qualities of the leather at the same time?

DR. MANN: No, we were merely trying to find out how resistant the leather was to penetration by water. We did not carry the test beyond a few minutes.

DR. ROBERT M. KOPPENHOEFER (Socony Mobil Oil Company): I take it from your presentation that you feel the most important aspect is the resistance of the leather to penetration of water, rather than to water take-up, or water absorption. Is that the conclusion you have reached as a result of your work?

DR. MANN: I feel that the leather for gloves should retain as many of its glove properties as possible and at the same time resist the penetration of water to the maximum. I feel that in shoe upper leather also the alteration in the usual desirable properties should be at a minimum, and that at the same time the resistance to water penetration should be at least high enough to last for several hours in a shoe.

Contrary to some belief, these highly resistant leathers have relatively high permeability to water vapor—many times higher than the old stuffed, retanned leather formerly used in military boots.

The famous Greek poet, Homer, describes his heroes as being clad in leopard skins, and in one passage he mentions a shield which was made "of sevenfold ox-hide." He also praises the half-boots of Agamemnon, the great commander of the Greek army at the siege of Troy. —*Leather and Bootmaking*, William J. Claxton. London and Glasgow: Blackie & Son Ltd.

AMINO ACID COMPOSITION OF DIFFERENT PROTEINS PREPARED FROM SKINS AND HIDES OF INDIAN ANIMALS

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ABSTRACT

The amino acid composition of collagen, reticulin, elastin, albumin, globulin, mucoids, myosin, and keratin was determined by two-way paper chromatography.

INTRODUCTION

Animal skin or hide contains about 90–95% proteins calculated on the basis of dry weight of the skin or hide. The important proteins of skins and hides are collagen, reticulin, elastin, and keratin, which are fibrous in nature; and albumin, globulin, and mucoids, which are non-fibrous, globular proteins. Besides these main proteins, the muscle fibers are made up of several proteins of which myosin is predominant.

The component amino acids of wool were estimated by microbiological methods by Graham, Waitkoff and Hier (1), and more recently by Simmonds (2), and Corfield and Robson (3) by means of column chromatography.

Estimation of most of the component amino acids of collagen was reported by Bowes and Kenten (4). The amino acid composition of collagen prepared from different sources was studied by Neuman (5), Eastoe (6), and Bowes, Elliott and Moss (7), using microbiological and ion-exchange chromatographic techniques.

Recently, Cassel (8) studied the amino acid composition of collagen by paper chromatographic methods.

Most of the component amino acids of elastin were estimated by Stein and Miller (9). Microbiological assays of amino acids in elastin were done by Neuman (5), and Graham, Waitkoff, and Hier (1). Recently, an amino acid analysis of elastin was made by Partridge and Davis (10) by ion-exchange chromatographic methods. No quantitative assay of the component amino acids of reticulin, albumin, globulin, mucoids, or myosin, prepared from skins and hides has yet been reported.

Recently, several new analytical techniques, e. g., paper chromatography and paper electrophoresis, have been developed for the amino acid analysis of proteins. Because of the availability of these new analytical tools, it was felt necessary as well as interesting to investigate the amino acid composition

of various proteins of skins and hides. A systematic investigation was therefore undertaken on the preparation of individual proteins in pure form from skins and hides, and on the complete quantitative analysis of each protein for component amino acids by means of the new technique of two-dimensional paper chromatography.

EXPERIMENTAL

The methods for the preparation of collagen, reticulin, elastin, keratin, albumin, globulin, and mucoids in pure form from skins and hides were standardized in this laboratory and outlined in a previous paper (11). These standardized methods were followed for the preparation of individual proteins from skins and hides for the present work. Collagen (11, 12) was prepared from the butt portion of a fresh buffalo hide. Reticulin (11, 13) was prepared from a fresh calfskin. Elastin (11, 14) was prepared from *ligamentum nuchae* from the neck of a cow, obtained fresh from the slaughterhouse. Keratin (11, 15), was prepared from the wool of a fresh sheepskin. Albumin (11), globulin (11) and mucoids (11, 12), were prepared from a goatskin which was obtained fresh from the slaughterhouse.

Myosin was prepared from the fleshings of a freshly flayed buffalo hide. The method followed was essentially the same as that adopted by Greenstein and Edsall (16) and by Bailey (17) in their preparation of myosin from rabbit leg muscles. The hide fleshings were collected immediately after flaying and were quickly brought to the laboratory. The material was minced as fine as possible in a meat mincer and was immediately added to five volumes of ice-cold salt solution containing KCl (0.5 *M*) and $NaHCO_3$ (0.03 *M*). The mixture was gently stirred in the cold for about two hours, and solid $NaHCO_3$ was added at intervals to maintain the pH at about 7.5. Any fat which separated out was removed. The clear liquid was decanted after centrifuging, diluted with twenty volumes of ice-cold distilled water, and brought to a pH of about 6.8 by adding dilute HCl with constant stirring. The myosin which was precipitated was separated by centrifuging and washed with cold distilled water. For purification, the washed material was redissolved in KCl and $NaHCO_3$ solution, centrifuged, and reprecipitated by dilution and acidification in the same manner as before. After centrifuging, the precipitate was washed with cold distilled water, dehydrated in alcohol, then in ether, and finally *in vacuo* over P_2O_5.

Each of the proteins thus prepared was subjected to certain color tests, viz., the Molisch test (18) and Hopkins-Cole test (19), and was analyzed for total nitrogen by the method of Chibnall, Rees and Williams (20) and for total sulfur by the Official Method of Analysis (21) as adopted by Bailey (22). Before analysis, each protein was finely powdered in a mortar and dried to constant weight in a vacuum oven at 100°C. The results are presented in Table I.

TABLE I

CHARACTERIZATION OF DIFFERENT PROTEINS PREPARED FROM SKINS AND HIDES

Protein	Total N	Total S	Molisch Test	Hopkins-Cole Test
Collagen	17.76	0.19	Very faintly positive	Negative
Reticulin	16.63	0.04	Negative	Negative
Elastin	16.84	0.31	Negative	Negative
Keratin	16.47	3.86	Negative	Positive
Albumin	15.25	1.88	Very faintly positive	Faintly positive
Globulin	15.61	1.08	do.	Positive
Mucoids	11.93	3.90	Strongly positive	Faintly positive
Myosin	16.58	1.17	Negative	Positive

50 mg. of the protein were weighed into a thick-walled Pyrex glass tube sealed at one end, 15 ml. of 6 *N* HCl (A. R.) which had been redistilled in glass three times were pipetted in, and the tube was evacuated to about 3 mm. pressure and sealed. The sealed tube was heated in an oven at 110°C. for 24 hours, which was sufficient to complete the hydrolysis. By this procedure, there was very little or no formation of insoluble humin, except in the case of mucoids. After the hydrolysis was completed, the seal was opened, and any insoluble humin was removed by centrifuging. Then the hydrochloric acid was removed by evaporation *in vacuo* at 40°-50°C. over P_2O_5 and KOH.

The dried residue was dissolved in 10 ml. of glass-distilled water and desalted in a modification of the apparatus devised by Consden, Gordon, and Martin (23) for the removal of inorganic salts from protein hydrolyzates. As soon as the desalting was completed, the solution was taken out, and the surface of the mercury cathode was rinsed two or three times with glass-distilled water. The solution and washings were mixed, concentrated to below 10 ml. *in vacuo* at 30°–35°C. and finally made up to 10 ml. with glass-distilled water. This solution was then analyzed for its component amino acids by a two-dimensional paper chromatographic technique which was previously standardized for the identification of twenty different amino acids by preparing the paper chromatograms of a series of mixtures of known amino acids.

The apparatus and general procedure adopted in the present investigation were based on the method described by Consden, Gordon, and Martin (24). The quantity of solution corresponding to 0.5 mg. of the protein hydrolyzate was spotted in small increments near the corner of Whatman No. 1 chromatography paper (18″ x 22.5″), the spot being air-dried after each addition. The paper was placed in position inside the chromatographic cabinet with the upper edge of the paper immersed in the developing solvent which was a

4:1:5 mixture of *n*-butanol, glacial acetic acid, and water (25) contained in a glass boat. The inside atmosphere was kept saturated with the solvent vapor. The chromatogram was allowed to develop for 24 hours. The paper was then removed, dried in air, turned through a right angle, and returned to the cabinet. The chromatogram was developed for 24 hours more by the second solvent mixture consisting of a pyridine-water mixture (26) (4:1). After air-drying, the paper was sprayed uniformly with ninhydrin solution (0.5% in 95% acetone), again air-dryed and then heated at 65°C. for 30 minutes to develop the colors. The spots were carefully outlined with a pencil. A number of control chromatograms of known quantities of mixtures of different standard solutions of twenty known amino acids were run simultaneously in the same apparatus under identical conditions. The amino acids present in the unkown protein hydrolyzate were identified by reference to the chromatograms of the known amino acids. In order to resolve any overlapping amino acids, e. g., leucine – isoleucine, cysteine – cystine, lysine – arginine, the above experiment was repeated using as the second solvent mixture pyridine – iso-amyl alcohol – water (26) in the proportion of 10:10:7, pyridine – amyl acetate – water (26) in the proportion of 2:1:1, or methyl ethyl ketone – pyridine – water (27) in the proportion of 14:3:3. The solvent mixtures were always freshly prepared from A. R. quality solvents redistilled in glass.

For quantitative estimation of the amino acids, the method of Giri, Radhakrishnan and Vaidyanathan (28) was followed with such modifications as were found to be necessary in the case of two-dimensional paper chromatograms. The individual spots of each of the control chromatograms which were obtained by using known quantities of known amino acids were cut out and eluted with 5 ml. of 75% ethanol containing 0.004% copper sulfate. The intensity of the color of the solution was determined using a Klett-Summerson photoelectric colorimeter with a green filter No. 54. A blank on the solution used for eluting the spots was subtracted from the readings. The standard curve for each of the twenty amino acids chromatographed was drawn by plotting the net colorimeter readings against the concentration of amino acid solutions used for spotting, and the straight line portion of the curve, obeying Beer's Law, was used for all further reference. In most cases, the linear relationship between the intensity of color and the concentration of amino acid was found over the range of about 3 μg. to about 11 μg. In five cases, viz., cysteine , cystine, methionine, hydroxylysine and hydroxy-proline, the linearity was observed over the range of about 1 μg. to about 7 μg. The standard curves for the chromatogram of a few typical amino acids are presented in Figure 1. The individual spots of the chromatogram of the unknown protein hydrolyzate were then cut out, eluted, and, if necessary, diluted to a suitable volume, and the intensity of the color of the solution was determined in the same manner. The quantity of each amino acid

was estimated by reference to the straight line portion of the standard curve of the corresponding amino acid. The values were expressed as g. of amino acid residue per 100 g. of dry protein.

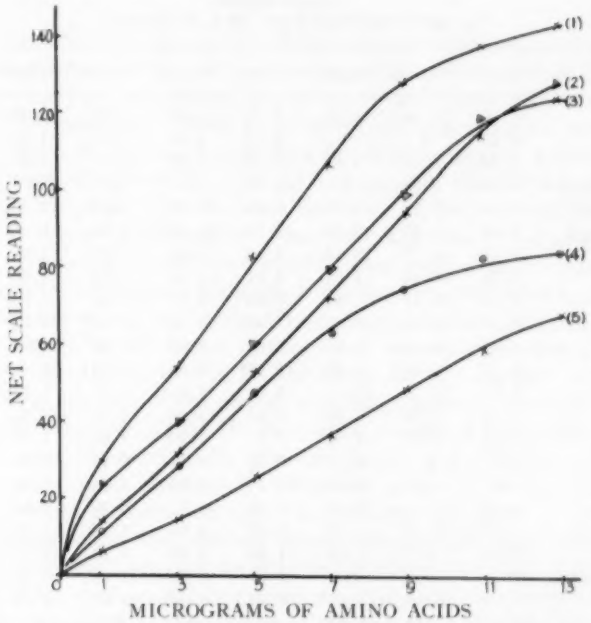

FIGURE 1.—Typical standard curves for colorimetric determination of amino acids. (1) Methionine; (2) arginine; (3) glycine; (4) hydroxylysine; (5) histidine.

The cysteine spots in the chromatograms for 24-hour protein hydrolyzates were found to be very indistinct. Cysteine has been reported (29) to be lost when acid hydrolysis of a protein is carried out for long periods. As cysteine, cystine, and a few other amino acids (29–31) are known to be preferentially liberated in the early stages of acid hydrolysis, cysteine and cystine were estimated separately from the chromatograms of solutions hydrolyzed for 12 hours.* As hydrolysis of a protein by acid is known (32) to result in the complete destruction of tryptophane, the proteins which gave a positive Hopkins-Cole test were analyzed for tryptophane independently by the method of Bates (33) as modified by Sullivan and Hess (34). The results are presented in Table II.

*Several investigators (10, 36, 43) estimated cysteine and cystine together by converting cysteine and cystine into cysteic acid by oxidation with performic acid. In the present investigation cysteine and cystine were estimated separately, using 12-hour protein hydrolyzates, as it was observed that considerable loss of cysteine occurred during hydrolysis for 24 hours. Kassell and Bran (29) also determined cysteine and cystine separately in different proteins (lactalbumin, edestin, papain, and casein) by hydrolyzing the proteins for the optimum time required. They observed that 8-hour hydrolysis of papain and lactalbumin with 6 *N* HCl at 140°C. was quite satisfactory for separate estimations of cysteine and cystine.

TABLE II

PERCENTAGE COMPOSITION OF AMINO ACIDS IN DIFFERENT PROTEINS PREPARED FROM SKINS AND HIDES

(*g. amino acid residue per* 100 *g. dry protein*)

Amino Acid Residues	Collagen	Reticulin	Elastin	Keratin	Albumin	Globulin	Mucoids	Myosin
Arginine	7.05	9.04	1.81	9.21	4.59	3.32	3.51	6.53
Histidine	0.67	0	0	0.63	3.06	2.04	1.84	1.87
Lysine	4.10	6.01	1.62	2.59	9.97	5.27	5.61	11.32
Hydroxylysine	1.06	0.68	0	0.32	0	0	0	0
Aspartic acid	2.68	5.52	1.10	6.22	9.12	7.35	12.37	8.54
Glutamic acid	5.01	8.35	3.96	13.58	13.81	9.94	8.05	21.86
Glycine	26.62	14.91	28.94	5.44	0.60	9.51	4.93	0.98
Alamine	9.14	10.46	4.01	3.11	1.74	1.03	1.99	2.97
Serine*	3.60	5.42	1.86	7.94	3.55	8.08	5.03	3.24
	(3.37)	(5.11)	(1.67)	(7.43)	(3.28)	(7.41)	(4.62)	(3.01)
Threonine*	1.47	2.61	1.98	5.63	5.02	7.65	4.92	4.68
	(1.36)	(2.44)	(1.83)	(5.41)	(4.80)	(7.33)	(4.69)	(4.50)
Valine	1.71	8.13	12.41	3.68	5.51	7.32	5.10	3.60
Leucine	3.22	4.50	12.93	8.02	13.09	7.05	4.92	13.11
Isoleucine	1.03	2.05	4.96	2.71	2.10	2.96	1.74	2.88
Cysteine†	0	0	0.41	0.56	0.41	0.44	0.47	0.37
Cystine†	0	0	0.53	13.20	6.03	3.11	5.51	0.95
Methionine	0.40	0	0.32	0.51	0.52	0.50	0.68	3.51
Phenylalanine	1.83	3.24	3.75	2.92	5.90	3.19	2.89	3.94
Tyrosine	0.74	0	1.44	4.68	5.12	7.24	4.51	4.17
Tryptophane	0	0	0	1.01	0.40	3.19	0.46	0.71
Proline	15.16	10.30	14.63	6.92	6.09	6.83	3.81	3.57
Hydroxyproline	13.12	7.44	2.53	0	0	0	0	0
Total	98.61	98.66	99.19	98.88	96.63	96.02	78.34	98.80

*The data are not corrected for losses of serine and threonine during acid hydrolysis. The data given in parentheses were obtained on 36-hour protein hydrolyzates.
†The data for cysteine and cystine were obtained on 12-hour protein hydrolyzates.

It is also known (32) that certain other amino acids like serine, threonine, etc., are partially destroyed on prolonged acid hydrolysis. In order to study the extent to which such amino acids were destroyed under the present experimental conditions and also to verify whether the period of 24 hours was sufficient to complete the hydrolysis of all the proteins studied, chromatograms were prepared for 36-hour protein hydrolyzates and the estimations of individual amino acids were repeated in the same manner as before. As no significant difference was observed in most of the amino acids between the data obtained on 24-hour and 36-hour protein hydrolyzates, the results for the 36-hour hydrolyzates are not given separately. In those cases where significant differences were observed, the results for 36-hour hydrolysis are

presented in parentheses under the date for the 24-hour hydrolyzates in Table II.

DISCUSSION

As the paper chromatogram for 24-hour hydrolyzates of each protein showed distinct spots for the different amino acids present, and as the data for all the component amino acids (except serine and threonine) obtained in 36-hour hydrolyzates were found to be essentially the same as, and in no case higher than, the corresponding data for 24-hour protein hydrolyzates, it may be reasonably concluded that the hydrolysis of the different proteins analyzed was completed after 24 hours under the hydrolytic conditions employed in the present investigation. Eastoe (6) also found that gelatin and collagen were completely hydrolyzed after 24 hours even under comparatively milder hydrolytic conditions. Although it has been reported that in the case of certain other proteins, viz., insulin (35), carboxypeptidase (36), papain (37) and ribonuclease (38), the release of valine and isoleucine is incomplete after 20–24 hours hydrolysis with 6 *N* HCl at about 105°C., no such difficulty was observed in the case of the present samples of proteins analyzed.

The results obtained (Table II) show that the samples of collagen and elastin contained 18 amino acids, whereas keratin and reticulin contained 20 and 15 amino acids respectively. Nineteen amino acids were found in each of the other proteins analyzed, viz., albumin, globulin, mucoids, and myosin. If the amino acid residues which were present in concentrations of about 10% or above are considered to be the major components, it may be seen that glycine, proline, and hydroxyproline are the major components in collagen; glycine, alanine, and proline in reticulin; glycine, proline, leucine, and valine in elastin; glutamic acid and cystine in keratin; glutamic acid, leucine, and lysine in albumin; glutamic acid in globulin; aspartic acid in mucoids; and glutamic acid, leucine, and lysine in myosin. The results also show that certain amino acid residues were present only in traces (concentrations of about 0.5% or less), viz., methionine in collagen; cystine, cysteine, and methionine in elastin; cysteine, methionine, and hydroxylysine in keratin; methionine, cysteine, and tryptophane in albumin; methionine and cysteine in globulin; cysteine and tryptophane in mucoids; and cysteine in myosin. The finding of a very small amount of hydroxylysine in keratin is in agreement with the work of Van Slyke *et al* (39), Middlebrook (40), and Simmonds (2), but it is in disagreement with the work of Hamilton and Anderson (41).

It may also be seen from Table II that glycine and proline occur in very large amounts in collagen and elastin; reticulin was also found to be fairly rich in glycine and proline. Among the eight proteins analyzed, hydroxyproline was found to be present only in collagen, reticulin, and elastin; and hydroxylysine only in collagen, reticulin, and keratin—the hydroxyproline

and hydroxylysine contents of collagen being the highest. The glutamic acid content of myosin, keratin, and albumin, and the leucine content of myosin, elastin, and albumin were found to be very high. Of the different proteins examined, the cystine content of keratin was found to be the highest. Histidine was found to be present in very small concentrations in collagen and keratin, and absent in reticulin and elastin. Reticulin was found to be deficient in sulfur-containing amino acids, viz., cysteine, cystine, and methionine; cysteine and cystine were absent in collagen also. The tyrosine content was found to be very low in collagen and nil in reticulin. The Hopkins-Cole test (Table I) gave negative reactions in the cases of collagen, reticulin, and elastin, which indicated that these three proteins did not contain tryptophane.

The data for the serine and threonine contents of each protein as obtained on 36-hour hydrolyzates were found to be lower than those for 24-hour hydrolyzates. The hydrolytic conditions of the present investigation were more or less of the same order as employed by Rees (42) who observed that the losses of serine and threonine were 10.5% and 5.3% respectively during acid hydrolysis for 24 hours. The results given in Table II have not been corrected for such losses of serine and threonine. If the correction factors of Rees are adopted in the present case, the figures for these two amino acids will be raised only slightly. It has also been reported (3, 36–38) that under much stronger conditions of acid hydrolysis of certain proteins, a few other amino acids like aspartic acid, glutamic acid, lysine, and phenylalanine were partially destroyed. However, under the comparatively mild hydrolytic conditions of the present investigation, no destruction of any of these amino acids was observed in periods up to 36 hours.

The results given in Table I show that of the different proteins examined, collagen had the highest nitrogen content, and mucoids the lowest. The sulfur contents of keratin and mucoids were found to be quite high, while reticulin was found to contain a negligible amount of sulfur. If the sulfur content is calculated from the sulfur-containing amino acids of the protein, it may be seen that in most cases there is a fair agreement between the calculated sulfur and the analytically determined total sulfur, whereas in other cases, e. g., mucoids and collagen, the analytical total sulfur content is higher than can be accounted for from the sulfur-containing amino acids. The excess sulfur may be derived from other sulfur-containing compounds which are known to be present in certain proteins; for example, mucoids are known (44, 45) to contain an appreciable amount of chondroitin sulfate.

The total content of amino acid residues was found to account for 98.6% to 99.2% of the total protein in collagen, reticulin, elastin, keratin, and myosin; 96% to 96.6% in albumin and globulin; and 78.3% in mucoids. Skin mucoids are known (44, 45), to contain about 20% carbohydrates, consisting of chondroitin sulfate, hyaluronic acid, glucose, galactose, and hexosamines. It has also been reported (46), that skin albumin or globulin con-

tains about 2.2% carbohydrate, consisting of mannose and galactose. Collagen also is known (47, 48) to contain about 0.65% carbohydrate composed of glucose and galactose. Recently, it has been reported (10) that elastin contains about 0.1% amino sugars. In the present investigation the Molisch test (Table I) gave strongly positive reaction with mucoids and very faintly positive reactions with albumin, globulin, and collagen. This indicated that a considerable amount of carbohydrate was present in mucoids and that the other three proteins also contained small proportions of carbohydrate. It may, therefore, be seen that if the carbohydrate content of the protein and also the losses of serine and threonine are taken into consideration, practically the whole of the protein has been accounted for.

SUMMARY

A two-dimensional paper chromatographic technique was fully standardized for the identification as well as for the quantitative estimation of 20 different amine acids.

Eight proteins of both fibrous and non-fibrous type (collagen, reticulin, elastin, keratin, myosin, albumin, globulin, and mucoids) were individually prepared in pure forms from skins and hides of Indian animals.

Each protein prepared was characterized by determination of total nitrogen and total sulfur and by certain color reactions.

Complete quantitative analysis of the component amino acids in each protein was carried out by means of the two-dimensional paper chromatographic technique.

The results obtained on the amino acid composition of the different proteins analyzed were compared and discussed.

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"EICHENKRANZ" REVIVED

The association of graduates of the German Tanning School at Freiberg, Saxony, known as "Eichenkrantz", has become active again. Annual meetings will be held in conjunction with the meetings of the German Association of Tanning Chemists and Technologists (VGCT). The following notice is published at the request of Mr. Dresen, of Reutlingen, who is anxious to reach all former Freiberg students, now scattered all over the world.

"The announcement of May 31, 1956, concerning the re-establishment of the Association of Old Members of the 'Eichenkranz' Society, brought together a splendid number of former tanning students at the time of the VGCT meeting in Freudenstadt. These gave the Association the assurance that mutual respect, professional solidarity, and a true comradely spirit still prevail among Freiberg graduates in all corners of the earth, and that they will strive to restore the former society. An ordinary meeting was held in Reutlingen on September 29, 1956. The first General Meeting will be held at Trier in 1957, in conjunction with the VGCT. For information and announcements, write to Mr. Dresen, Hindenburgstrasse 15, Reutlingen, Germany."

DISCUSSION OF THE APPLICATION OF COLORANTS TO LEATHER

The following discussion followed the presentation of papers by Messrs. Stubbings, Casnocha, Geister, and Kirk, at the Perkin Centennial in New York, September 11, 1956. These papers were published in *JALCA*, **51**, 514–29 (1956).

CHAIRMAN COMPTON: In the preceding panel discussion of the Application of Colorants to Leather, Dr. Stubbings briefly outlined the chemical and physical reasons for the somewhat empirical procedures that are presently employed in this field. Mr. Casnocha and Mr. Geister discussed the major conventional techniques of through-coloring and surface-coloring. Dr. Kirk then described some of the new techniques by which greater light-fastness and wash-fastness characteristics are imparted to leather. In general, these techniques involve the through-coloring of the stock. Certainly such a broad presentation as this panel has given, in so brief a time, must give rise to many questions. I am sure the panel will be glad to answer them.

DR. SELIGSBERGER: I would like to ask Dr. Stubbings whether the differences observed in grain dyeing, which he showed on the screen, are limited to one or another class of dyestuffs, or are they common to all?

DR. STUBBINGS: The only dyestuffs that we investigated by this technique were the normal acid and direct dyes used in dyeing chrome leather.

We can't see any reason, from the molecular structures of the dyes or their molecular weights, why these materials should show these differences in properties. We have not gone far anough to be able to say much about it. I am sorry we didn't investigate any types of dyes for penetration other than the acid and direct.

QUESTION: Why is it that some leathers show differences in color on the grain and flesh sides in ordinary drum-dyeing?

MR. GEISTER: Some classes of dyes will dye the grain better than the flesh. The rapid exhausting type of dye is inclined to dye the grain side more than the flesh side. The slowly exhausting type will be inclined to dye the flesh side stronger. Sometimes, the grain cannot be rewet after crusting for dyeing. The leather dyer is sometimes frowned upon by the textile dyer because he may use as many as eight or ten dyestuffs for a shade. It is necessary to dye the front, the back, and the middle. You are sometimes forced, in order to get a certain shade and grain, to use one dye on one side, another dye for the middle, and still another for the other side.

QUESTION: What influence, if any, is exhibited by various neutralizing agents on the penetration of dyestuffs?

MR. CASNOCHA: As far as the cations are concerned, there is no appreciable difference between them. From a practical coloring standpoint the same results are obtained whether we use sodium, potassium, or ammonium salts, even though some observations have been made on the change in the quality of the leather when ammonium bicarbonate is replaced with sodium bicarbonate. There is some difference in the leather itself, not in the color.

The nature of the anions has a much greater significance. Weaker shades with better penetration are obtained when we use phosphates or salts of some of the sulfonic acids. There does not appear to be much difference between borax and sodium bicarbonate, which are the two most widely used neutralizing agents. Yet there is a reference in the literature in which it is stated that some tanners prefer to use borax for blacks and bicarbonates for colors.

DR. TURLEY: I would like to ask Dr. Kirk a general question, since he has emphasized the trend to light-fastness, resistance to washing of leather, and resistance to dry cleaning. In today's markets, how fast do we have to make leather to light? Is it a question of making it with absolute fastness? How completely resistant do we have to make leather to washing with any kind of detergent or soap? And how completely must leather resist dry cleaning with any number of solvents? I think it would be interesting to bring that out. I have a feeling that in some cases it is almost impossible to make leather perfect—so that it is capable of resisting everything.

DR. KIRK: I think that is a double-barreled question. But it is a very pertinent one, too. I think I can answer that, to a certain extent, it depends entirely upon the use of the leather.

I am going to break this answer into three categories: (1) light-fastness, (2) dry cleaning or solvent-fastness, and (3) washing.

In glove leather, light-fastness is relatively unimportant. I ought not to say it that way, but it is certainly a minor factor for one fundamental reason: A pair of gloves is not going to be exposed to light in the same way as something worn on one's back out on the golf course. So you need only a relatively low order of light-fastness in glove leather. But by the same token, a garment —let us say a suede jacket—which will be worn in the bright sun on the golf course, should have a much higher degree of light-fastness. The upholstery for a car that is going to be exposed to intense radiation should have as high a degree of light-fastness as possible.

We have more or less gone over that field, especially with the glove tanners and garment leather people, and set up certain arbitary limits.

For glove leather, a dye that will resist ten hours of exposure to Fadeometer conditions is deemed sufficient. But the wash-fastness should be as good as in textiles, and for one fundamental reason: The woman who wears a pair of pink or aqua gloves is going to wash those gloves in the evening in

the hotel room, and will use soap and water to wash them. So they have to be fast to soap and water.

When we talk about the washing of leather and the fastness to washing required, the No. 2 A test of the AATCC seems to me to be absurd because —speaking of glove leather now—the wash-fastness you are talking about is what you need if you take a cake of Ivory soap and smear it over the gloves, and wash them in the sink or basin in a hotel room or your home. That is a different degree of fastness from a laundry-fastness which is required when something is sent to the laundry. No one, I believe, in his right mind, would send a $70.00 suede jacket to the laundry. I would not, and I don't think anyone in this room would. But we have made lots of garments (and they are still being made today) which can be thrown into the Bendix washer and washed without any deterioration of color. Those garments can be washed side by side, the green with the red and other combinations, and washed repeatedly without loss of color. That to my mind is sufficient fastness to washing.

When you come to the upholstery field, such as in a car, you are not going to send the upholstery to the laundry. You are not going to send it to a dry cleaner. But certainly if it is in a sports car, which is where most of the upholstery leather goes, you will expose it to intense radiation.

For that reason we broke down our requirements to fastness. For glove leather we arbitrarily set ten hours with no change in shade in the Fadeometer; twenty hours for the suede jacket; and thirty hours for grain leather. The suede itself tends to offset any slight reduction in color. But for upholstery leather, the minimum would have to be about 100 hours. In fact, I believe the requirement is 120 hours.

Actually, for my money, there is not a lot of difference between the color that stands 100 hours and one that stands 150 hours. Our experience is that when we had a dyeing that showed no break at 100 hours, it would frequently run to 200 hours with very little change. The break comes, usually, in the first 50 hours.

For that reason, we set these arbitrary limits, and they are purely arbitrary. But I think we've got to recognize that we are dealing with leather and not with cotton. We are not dealing even with wool. We are dealing with collagenous tissue which has been converted to leather, and leather is still our interest.

When we speak of textile-fastness, or fastness equal to textiles, there should be limitations placed on that, and I place one on it: Leather is a luxury item, and we handle it as a luxury. It is not something we purchase in the five-and-ten-cent store, or something we handle without discrimination. It is the quality of leather with which we are concerned.

CHAIRMAN COMPTON: I would like to add a little to that. With regard to upholstery leather, I doubt that in the automotive industry the volume of

leather used in sports cars is as great as that in hard tops. However, the upholstery tanner does have a problem, the 120-hour Fadeometer specification is based on upholstery leather with pigments in the finish—not dyestuffs. In regard to dyed leather for automotive use, there is a tendency to apply the leather specifications to a material that is more like a textile.

QUESTION: I think this question is somewhat like the one that Dr. Turley asked. Last year and this, we have seen in department stores articles of women's wear made of wool, nylon, or rayon, trimmed with leather. Are those leathers which have been particularly guided by your industry into that end use? Or are those leathers with ten-hour light-fastness and rather poor dry cleaning qualities? We are deeply concerned with those, and we recognize them as being a possible source of customer irritation against leather, if those leathers don't stand up in service and in cleaning. What attempt has been made to guide the high quality and good serviceable leathers into that use?

DR. KIRK: I think I can answer that to a certain extent. We handle the dyes; we don't make the leather. But I can say this: The dyes are available, or could be available, that would stand the rap. There is no excuse for the leather industry to foist something on the customer and say that it will stand up, when it won't. It can be made to stand up. Those leathers will cost more to dye. But if the tanner can stand the cost of the dyeing of the leathers, the properties you speak of can be secured. I agree with you, and I share your concern, that in the tremendous onrush of dyeing of leather today, a lot of it probably falls far short of the goals that can be reached.

CHAIRMAN COMPTON: There are one or two other tanners in the room. Would they like to speak on this question? It is the old problem of not considering the end use that causes the concern of the gentleman who just spoke.

MR. THORSTENSEN: I might interject a remark here on behalf of the industry. I know that no reputable tanner will sell his product for an improper end use.

DR. SOMERVILLE: Mr. Geister touched on the classes of dyes that might water-spot. I wonder if he could elaborate on that as regards the possibility of their migrating in finishing the leather.

MR. GEISTER: In cases where you have leather that may be steamed in forming it into shoes, or where you have finishes that tend to dissolve the coat below the one being applied, it is desirable to use a color which will bleed the least in water, or spot. Most insoluble dyes are spirit-soluble types. The only real objection to them is that they are not as strong as the water-soluble basic dyes. They are also sometimes avoided because of the effect

of solvents on surface oils in the leather. This fault can be overcome very well by including some oils in the dye coat.

DR. SELIGSBERGER: I would like to come back to Dr. Kirk's remarks and ask him to say a few words about solvent-fastness and the relative importance of solvent-fastness versus soap-fastness.

DR. KIRK: Well, it depends again upon the use. In glove leather solvent-fastness has very little direct significance. The primary interest is in fastness to soap and water. In garment leather, on the contrary, probably it is much more important to have solvent-fastness than soap-fastness. However, "dry cleaning" is seldom "dry". The dry cleaners usually add a certain amount of soap and water to the solvent. So, a dye which is strictly fast to an organic solvent is not necessarily fast to the present techniques of dry cleaning. Thus, I would say that dry-cleaning-fastness is by far the most important fastness requirement in garment leather. You must also have reasonable fastness to soap and water.

I do want to clear up one thing in connection with what Mr. Thorstensen said. I don't mean to infer that the tanners have anything to do with the use of unsuitable leather for certain purposes. After the tanners make the leather they have very little to do with the fabrication of the leather into the finished article. So the tanners are somewhat the victims in this respect. "A" may be making a leather very highly resistant to soaping, solvents, and sunlight, but when he sells his leather he no longer has control of that leather. There is nothing to stop that leather from being mixed with "B's" which is quite inferior, and "A" gets a black eye from that angle. I think that is the real danger.

MR. THORSTENSEN: Dr. Kirk, wouldn't that then get back to the stylists who say, "We want this"—and that is it?

DR. KIRK: If the stylist would come forward and say, "This is what we want", and convince the consumers that they can get it, and if the manufacturers would say, "We will pay the difference for making this leather", there would be no reason why the leather garment should not last as long as a textile garment.

QUESTION: Is the leather industry making any effort to give information needed by the customer on the label, so that we may note that we are getting a good product from the tanner? Is there any chain coming down from the tanner to the customer on this?

DR. KIRK: We can carry on a certain amount of the promotion from the standpoint of what can be done. But that is where the supply end stops. It goes back to getting the consumer aware of the fact that he can get the thing if he demands it.

MR. SALAMATOV: I would like to address my questions to Mr. Casnocha. He was talking about the penetration of dyes and the molecular size. We seem to be confronted with molecular size all the way. In tanning we can achieve certain results by manipulation of the size of the molecules. Can you do that in the same way in dyeing, or is that one thing that is not yet practical?

MR. CASNOCHA: To a certain extent it is possible and practical, but as we enlarge the molecules of the dyes we change their color. For example, black dyes have more complex molecules than yellow dyes. Consequently, there are no jet black dyes that penetrate as well as some of the yellow dyes. However, there are other factors in addition to the molecular size that enter into the picture. Even though a dye might have a large molecular weight, it might also contain a number of sulfonic groups, or they might be placed in such a position that they would counteract the influence of the molecular size itself. Thus, investigators who originally placed all emphasis on the molecular size as the factor responsible for penetration, are now changing their theories, because there appear to be other factors, in addition to molecular size, that influence penetration.

MR. RETZSCH: What is the panel's viewpoint as to the manner in which fat liquors affect the dyestuff—particularly some of the newer cationic and anionic fat liquors? How do they affect penetration, depth of shade, and so forth?

MR. CASNOCHA: The effect of fatliquoring depends on the type of fat liquor and the dyes which have been used in coloring. The dyes that have a low affinity for leather are displaced or stripped more easily than dyes that exhibit greater affinity. The anionic types of fat liquors, which are usually sulfated oils, will be more effective strippers as we increase their SO_3 content. Oils which contain free alkali will strip the dye more than oils which are neutral or somewhat on the acid side.

As to the cationic fat liquors, there are such differences between them that it is difficult to predict their behavior. In the main, they appear to intensify the shades. In certain instances, especially when bleeding dyes are used in coloring, we encounter difficulty with so-called "picture frames". The anionic dyes bleed out of the leather, precipitate with the cationic oils, and then redeposit either on the flesh side or in the loose area of the grain.

The nonionic types of fat liquors have the least influence on the penetration and shade of the colored leather.

MR. TURLEY: I would like to address a question to Dr. Stubbings. Getting back to the chemical side, he pointed out the number of polar groups, and the difference in effect on collagen and on wool. However, in nature the collagen is certainly quite different from wool. In collagen, the basic protein

combines naturally with the acid dyes. Perhaps wool is an anionic protein. Have you come across any information as to what makes that truly profound difference? It is a great difference. The dyeing of leather could never be approached in the same way as the historic dyeing of wool. But secondly, we were intrigued many years ago, in studying the histology of leather, by the effect of retanning. It seemed to enhance the natural affinity of collagen for the acid dyes. Is there any evidence that that is what is happening, or does the dye have some affinity for the chrome? If we could know more about that, we could have a better idea of what is happening in a straightforward dyeing process.

DR. STUBBINGS: In partial answer to your first question about the difference in wool and collagen, actually wool has structural aspects which we don't consider when we look at its chemical nature. Wool is not a homogeneous material either. It has a sheath, and that sheath is penetrated by different means. I think it is probably the sheath on the wool fiber compared with practically no sheath on the collagen fiber that makes the biggest difference of all between the two. Chemically they are much alike in terms of their protein nature except for the cystine that forms S-S cross-links in wool.

In addition to that, wool can be dyed, and normally is dyed, at a much higher temperature than is leather. Collagen fiber won't stand high temperatures; raw collagen will stand up to 50°C. and above that it shrinks. The wool will stand practically steam temperatures. That alone makes for tremendous differences in the practical dyeing of the two.

The slide* that I showed shows the greater affinity of dye for chrome-tanned fiber, in terms of milliequivalents of dye absorbed per gram of fiber, than for raw fiber.

We made many studies in an attempt to find out whether what you are asking is true or not—whether there is an increasing affinity of the fiber for the dyestuff or a dyeing of the chromium—the reaction of the dyestuff with the chromium molecule.

I don't think there is much doubt that the increase in affinity of the dye for chrome-tanned fiber is due to the chromium and not the fiber. The raw fiber takes up a maximum of about 0.9 milliequivalents of acid dye per gram of fiber. We get on as much as 2.5 or 3 milliequivalents of dye per gram of chrome-tanned fiber. It would be almost impossible to postulate realistically that parts of the fiber could be binding that additional dye because certain groups are freed or opened up. So I believe that it is quite definite that the chrome itself is combining with the dyestuff to produce the additional affinity shown in the slide*

MR. SHEPARD: I would like to ask this: What is the difference between dyeing and staining, and do you think that leather is dyed, or stained, or a combination of both?

*JALCA, **51**, 517 (1956).

MR. GEISTER: My interpretation is that staining is coloration in such a manner that the color is not combined and will easily bleed out again, whereas dyeing is a permanent coloration or chemical combination with the fiber. Sometimes in staining prior to finishing side leather, some dyes are applied to the leather which will readily bleed out again. To my mind that is a true explanation of staining.

MR. CASNOCHA: My interpretation of staining is "coloring" that takes place only partially—we get a weak shade even though we have used an excess of color. The fiber shows limited affinity for the dye. I believe the textile fellows talk about staining when they color a mixture of different fibers. In some cases a small amount, or a fraction of the dye, is absorbed by one of the particular fibers, while the great majority of the dye reacts with another fiber. The particular fiber that holds the smaller percentage of the dye is considered to be stained, while the other fiber which took up a large share of the dyestuff is actually colored. That color is much faster to bleeding than the color of the stained fiber.

DR. STUBBINGS: Most practical leather dyeing colors only the surface of the leather; we are not interested in getting the dyestuff to penetrate and the result is almost complete take-up of the dye in twenty to thirty minutes in the dye bath. There is never any dye left over, or practically none. I think this indicates that we mean, by dyeing, a kind of chemical combination. I don't know what you mean by staining. But I would say in general there is a good chemical combination of the dyestuff with the leather, and it is rather rapid.

DR. KIRK: If you take an oil-soluble dye, which has no affinity group, then I think you have essentially staining. And I want to go back and comment on something that Dr. Turley said about dyes and combinations. If a dyestuff has an ortho-orthoprime hydroxy structure adjacent to a diazo linkage, you can couple chrome across that cross-linkage. Or, you might have a hydroxyl group adjacent to a carboxyl group; then you will get chelation of your chromium. A lot of dyes have that structure. If you raise the temperature sufficiently, the chrome definitely becomes linked through a nonionic link to the dyestuff. If your dyestuff has a hydroxyl group ortho to a carboxyl group, and forms a chelate with the chromium, then the dye becomes bound to the chrome structure, and that I think accounts for the fastness.

As a matter of fact, on a lot of chrome dyes if you could force the chrome in, you would get very fast dyeing. We have done dyeing with chrome colors at 180°F. to 190°F. I don't know what the effect of that would be in a tanning drum, but you would get much faster dyeing. It is possible to get extreme fastness on those chrome colors if you force the reaction. But you can't do

it under tannery conditions—except with a few colors. However, I think this is not actually staining; I think it is dyeing.

COMMENT FROM THE FLOOR: Two questions have arisen which I would like to answer partly: the question brought up by the textile group about labeling leather, and the properties of leather which might be comparable to those of textiles. About a year ago someone went to our office, picked out some glazed kid, and said, "This is exactly the texture and quality and feel, and so forth, that we want. We want to put it around collars of suits or dresses and make them interesting for style purposes." As soon as the problem came to us, the technical people had some misgivings, but we were immediately assured that we could relax because these cuffs or other ornamentations would be removed, or the customer would be told to remove them, before they were sent to cleaners or before anything else was done to the garment. Because of that, the technical people rested at ease.

I might add that most leather has been made primarily for shoe purposes, and the textile people should be specifically told this. If they want to use leather for other purposes, it is up to the leather industry to try to meet their requirements and still retain the leather qualities which are desired.

CHAIRMAN COMPTON: If there are no other questions, I should like to ask Mr. Thorstensen, President of the American Leather Chemists Association, to close this panel discussion.

MR. THORSTENSEN: It has been a pleasure for ALCA to present a panel here on dyeing of leather. I have been in this business only a few years, but the leather industry is probably, outside of agriculture, the oldest in the world. According to the Bible, there were two people, Adam and Eve, and the first thing they did was to get something to eat. As for clothing, Eve needed nothing but a fig leaf. She soon found that was not adequate and that it was necessary to use the covering of animals. Those didn't last very long until some way of preserving them was found.

So with the leather industry as old as it is, and primarily not a manufacturing industry—it is purely an industry that converts a by-product of one industry into the raw material of another—we have gone through the years trying to improve the techniques by which leather is made. The session here today is concerned only with the coloring of this leather. But I believe the lady who asked the question about labeling a while ago is entitled to an answer.

There are many, many types of products made of leather, and there are many types of leather. If you think of all the different animals in the world that have skins that can be converted into leather, they all represent different problems to the tanner, and different problems to the colorist and to the experts in dyestuffs. The leather industry is purely an industry of conversion,

and consequently the materials we use as colorants must be produced by what we call the allied industries or the suppliers. They have done a terrific job, especially in the last few years, in making better and better dyestuffs. The tanner, through his research programs, has developed better and better leather. But man's concern remains: "What do I have to pay for it?" or "How much is it going to cost?" Consequently, the industry has to produce leather that will make shoes that will sell for $1.98, and shoes that will probably sell for $26.00. You can make garments that will sell for four to five dollars, and you can make garments that will sell for over a hundred dollars. It is simply a matter of what people will pay for them.

As Dr. Kirk brought out, these new techniques that make washable and dry-cleanable leathers cost a great deal more than those which do not.

We have seen instance after instance in the industry where people said, "Why keep on with this when every time we go out to sell a good product they use the price hammer on us?" And we have heard one tanner after another say, "Let George do it—I am going to get out while the getting is good." So if you want these good qualities, you are going to have to pay for them. Any producer who has not the nerve to ask a fair return for a good product has no business going out just to say, "Well, it is leather." There are just as many different kinds of leather as there are textiles.

Hides and skins are among the most complex of natural fibers. We have man-made fibers that are wonder fibers, just as we have wonder drugs. But when we come to natural fibers, the most complex and useful are those produced in the skins of animals. They produce a luxury item that has better properties than any artificial fiber that can be produced. If you will look into your history and into your museums, you will find leather used before there were textiles or plastics or anything else, and some of these ancient leathers are still in serviceable shape.

I hope that you who are not a part of the leather industry itself will remember that you get exactly what you pay for in leather, whether it is in garments, or handbags, or shoes, or what have you.

Editors as well as laboratory workers are subject to Murphy's Laws, to wit:
I. If something can go wrong, it will.
II. When left to themselves, things always go from bad to worse.
III. Nature always sides with the hidden flaw.

—*Scientific American, April,* 1956.

Dr. K. W. Pepper, Deputy Director since 1953, will become Director of the British Leather Manufacturers' Research Association Laboratory upon the retirement next January of the present Director, Dr. Henry Phillips. Dr. M. P. Balfe will assume the position of Deputy Director while retaining his post as nead of the Liaison Department.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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The Annual Index will be issued this year as a separate brochure. It will be mailed to members in early January.

$1,000 PRIZE FOR OUTSTANDING PAPER

The American Leather Chemists Association is offering a prize of $1,000 for an outstanding paper to be presented by the recipient at the next meeting of the International Union of Leather Chemists' Societies, in Rome, in September, 1957.

The paper must be an original contribution, not previously submitted for publication, in the general field of leather chemistry, either pure or applied. All active members of the Association are eligible to compete for this prize. A detailed abstract of each paper to be submitted must be mailed to the Secretary of the Association in Cincinnati (*not* to the Editor) not later than January 1, 1957. The complete paper, in final form for presentation, must be mailed to the Secretary by March 1, 1957.

Selection of the prize-winning paper will be made by the Awards Committee, consisting of Messrs. Robert G. Weldon, Carl G. Telander, and Ralph Porter.

OBITUARY

B. M. DAS—1886–1956

Rai Bahadur B.M.Das, M.A. (Calcutta), M.Sc. (Leeds), Director of the Central Leather Research Institute, Madras, died on September 6, 1956, following a coronary thrombosis. His death is a grievous loss to the science of leather chemistry, to the leather industry of his native country, and to the Institute that he headed.

Professor Das had a long, active, distinguished, and exceedingly varied career. After graduating with honors from the Presidency College, Calcutta, he was granted a research scholarship and worked on the chamber process of manufacturing sulfuric acid. He was the first to put sulfuric acid manufactured in India on the commercial market. On completion of this research, he was awarded a scholarship to study at Leeds under Professor Edmund Stiasny. His master's thesis, on the chemistry of the second bath of the two-bath chrome-tanning process was a notable contribution to our understanding of this complex process, and was to be followed by scores of papers dealing with almost every phase of leather chemistry and technology.

He was coauthor of a paper appearing in this issue.

After leaving Leeds, he was employed successively by a large Italian tannery and by Farbenfabriken Fr. Bayer. Returning to India after five years in Europe, he became Manager of the National Tannery, Ltd., Calcutta. This position he held for about 24 years, during which time the tannery was modernized and greatly expanded. While still manager of this tannery—a job which most men would consider all that they could undertake

—he was instrumental in establishing the Bengal Tanning Institute and served as its Superintendent for nineteen years. Both at the tannery and the Institute he carried on a great deal of research directed toward the modernization of the Indian leather industry and the improvement of its product. The Government of India recognized his services by awarding him the title of Rai Bahadur and also the Silver Jubilee Medal. In his later years, his talents were increasingly utilized by the Indian state and national governments in planning for the development of the leather industry during the post-war period. He took part in the British Intelligence study of the German tanning industry in 1946 and also spent some time in Great Britain and the United States. From 1951 on he was associated with the Central Leather Research Institute, Madras, of which he became Director in 1953. He also held the title of Professor of Leather Technology and Chairman of the Faculty of Technology, University of Madras.

Through his scientific and technical publications, Professor Das contributed much to the advancement of the leather industry of India. His greatest, and most lasting contribution, however, is the men whom he trained in the schools and laboratories which he founded or developed. These men, now holding important positions throughout India, will carry on his work. Through them his influence will be felt for many years to come.

COUNCIL MEETING MINUTES

JUNE 17, 1956

Grand Hotel
Mackinac Island, Michigan

The meeting was called to order at 9:15 P. M. Present were Messrs. Compton, Maeser, Thorstensen, Merrill, Flinn, Meo, H. R. Miller, Wederbrand, Weldon, and O'Flaherty.

E. B. Thorstensen as Coordinator of the Technical Committees presented a report which is to be completed, and since it contains the recommendations of all committee chairmen regarding changing the status of the present provisional methods, it will be submitted to the members at the business session. Council then agreed that the final action should be published in the Journal.

Dr. Stubbings proposed in a motion that, in the future, methods should have published with them reference to the committee work concerned. This was seconded by M. Maeser and carried.

H. Miller reported briefly on the convention arrangements.

Council agreed that abstracts of papers being presented could be released to the press after they are approved by the Editor-in-Chief, H. Merrill.

O. Wederbrand reported on the exhibitors and the location of their exhibits.

E. D. Compton reported on the Perkin Centennial, advising that the panel would consist of:

Dr. R. Stubbings
Mr. Jos. Casnocha
Mr. C. H. Geister
Dr. J. S. Kirk

The papers are to be published simultaneously in the Journal and in the Centennial Book.

Dr. Compton is to furnish the Secretary copy for publication in the Journal and then releases to the press.

M. Maeser reported briefly on the organization of the A.S.T.M.-A.L.C.A. Committee. He reported much interest and good attendance at the meetings.

Dr. Flinn presented to Council the following memorandum of agreement covering the arrangements made concerning the editorship of the Journal.

"The following defines the position, remuneration, and area of performance of the Editor-in-Chief and Managing Editor of the A.L.C.A. Journal.

"*Editor-in-Chief*

"1. Approved by Council action, the position of Editor-in-Chief for the Journal of the American Leather Chemists Association has been created. (Dr. Henry B. Merrill has accepted the post as first Editor-in-Chief).

"2. It is understood that the position of Editor-in-Chief shall be filled by a member of the Association as appointed by Council. He shall serve a three-year term and will not be eligible to succeed himself.

"3. It is understood that the Association will pay a total of $600.00 per year for the services of the Editor-in-Chief. Payment is to be made by the A.L.C.A. Secretary-Treasurer on a monthly basis on receipt of vouchers submitted by the Editor-in-Chief.

"4. It is understood that incidental expenses, not to exceed $400.00 per year (amount subject to change each year by Council action) will be assumed by the Association. These incidental expenses are those attendant to the operation of the office of Editor-in-Chief. Such expenses include stationery, postage, telephone and telegraph, and traveling. Reimbursement of such expenses will be made by the A.L.C.A. Secretary-Treasurer on a monthly basis on receipt of vouchers submitted by the Editor-in-Chief.

"5. It is understood that the Editor-in-Chief will appoint an Editorial Board of a sufficient number to serve his needs and this Board will be approved by Council.

"6. It is understood that the Editor-in-Chief will determine the general policies of the Journal, assisted by the Editorial Board, subject always to the approval of Council.

"7. It is understood that the Editor-in-Chief performs all the functions that require a knowledge of leather chemistry. In his duties, the Editor-in-Chief will be responsible for screening technical articles submitted for publication, for correspondence with authors regarding papers and for transmittal of material to be published to the Managing Editor.

"8. It is understood that the Editor-in-Chief will be responsible for determining those journals to be abstracted, for making arrangements with the abstracters, and for screening the abstract copy. Similar responsibility applies to book reviews and translations. The budget for these functions is $400.00 per year (amount subject to revision each year by Council action). Reimbursement will be made direct to abstracters, reviewers, or translators by the A.L.C.A. Secretary-Treasurer on written advice by the Editor-in-Chief.

"*Managing Editor*

"1. Approved by Council action, the position of Managing Editor for the Journal of the American Leather Chemists Association has been created on a trial basis. Effective March 6, 1956, Professor Earl Joseph Watt, Coordinator of Special Services at Lowell Technological Institute, will serve as Managing Editor for the period of one year.

"2. It is understood that the Association will pay a total of $2500.00 during the one year for the services of the Managing Editor and any assistant(s) that he employs. Payment is to be made by the A.L.C.A. Secretary-Treasurer on a monthly basis on receipt of vouchers submitted by the Managing Editor.

"3. It is understood that incidental expenses, not to exceed $300.00 per year, will be assumed by the Association. These incidental expenses are those attendant to the operation of the office of Managing Editor. These expenses include stationery, postage, telephone and telegraph. Reimbursement of such expenses will be made by the A.L.C.A. Secretary-Treasurer on a monthly basis on receipt of vouchers submitted by the Managing Editor.

"4. "It is understood that the office space for the Managing Editor will be provided, free from charge to the Association, by Lowell Technological Institute.

"5. It is understood that the Lowell Technological Institute, through the Office of the President, Martin J. Lydon, has agreed to the participation of Professor E. J. Watt as Managing Editor of the A.L.C.A. Journal.

"6. It is understood that the Managing Editor will be responsible to the Editor-in-Chief and that he will have duties normally pertaining to a managing editor, namely all phases of publication from the preparation of the copy for the printer to the reading of the final proofs. This includes editing the copy for spelling, punctuation, and grammar, determining the make-up of each Journal issue, layout, and proofreading. He, and he alone, shall deal with the printer, except as decribed below.

"7. It is further understood that the Managing Editor's duties shall exclude all responsibility for Journal distribution, advertising (A.L.C.A. Secretary forwards copy to printer), business matters (A.L.C.A. Secretary handles all contracts with the printer and pays the bills), or determination of the technical quality of papers submitted.

"8. It is understood that printing will continue to be done at the Easton Printing Company unless Council dictates otherwise."

After careful consideration, it was moved by D. Meo and seconded by R. Stubbings, that this agreement be submitted for signature to the Editor-in-Chief, the Managing Editor, and President Flinn. The motion was carried.

Dr. Merrill reported briefly on the Journal. He advised that there was a shortage of papers for publication. He requested comments on the last two issues of the Journal.

Mr. Wederbrand recommended that the new Council consider an increase of advertising rates. The printing cost of the Journal was increased 13% at the beginning of 1956. This matter will be referred to the new Council.

The matter of a more suitable compensation for the Editor-in-Chief was discussed. It was moved by Mr. Meo and seconded by R. Weldon that the matter be tabled. The motion was carried.

Dr. Stubbings presented upon behalf of his committee the following report on giving special consideration to foreign members serving on Council.

"Dear Mr. President: The Committee which you appointed to study the possibility of including a special Canadian or foreign member on Council has studied the problem and through mail correspondence has arrived at a recommendation to Council. Our recommendation is unanimous in intent as to the primary question.

"We recommend that no action be taken at the present time by the A.L.C.A. Council to include as a special consideration any Canadian or South American or other foreign member of Council. Two of us feel that it might be a good idea for the Council to ask the President-Elect as coordinator of the technical committees to encourage foreign participation in our various committees, but at the present time we see no need for action beyond this. The third member of our Committee does not feel that we should even give any special consideration to the appointment of foreign members to our various working committees."

A motion to accept and approve the report was made by Mr. Meo and seconded by Mr. Thorstensen. The motion was carried.

The matter of papers being submitted for presentation at the International Union of Leather Chemists Societies by the committee is to be publicized; Mr. Weldon, chairman of the committee, will prepare copy.

The Secretary read an announcement from Mr. Suzuki advising that an association of Japanese Leather Technologists has been organized. Council requested that the Secretary send them a copy of our methods, by-laws, and an exchange copy of our Journal.

Dr. Flinn appointed the following Board of Tellers:

John Highberger, *Chairman*
Thomas Blair
Ira D. Clarke

The following new members were accepted to active status: Stanley E. Antos, Marjam G. Behar, Irving Braum, Russell P. Doyle, Jacques Giguere, Dionisio Gonzales, Howard Gottlieb, Richard Jenkins, Frank L. McGowan, John H. Porter, William J. Rau, and Herman P. Wagner.

Mr. Weldon advised that many of the Associations send their secretary to the International Union of Leather Chemists Societies meetings, and he recommended that our Association should send our secretary. The matter will be referred to the new Council.

Dr. Flinn expressed his appreciation of the cooperation and work of Council.

The meeting was adjourned at 11:30 P. M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary.*

COUNCIL MEETING MINUTES

JUNE 20, 1956

Grand Hotel
Mackinac Island, Michigan

A meeting of the new Council was called to order at 9:00 A. M. by President E. B. Thorstensen. The following were present: Messrs. Maeser, Stubbings, Compton, Lord, Miller, Weldon, Merrill, Flinn, Wederbrand, and O'Flaherty.

The minutes of the meeting of June 17 were read and approved.

The Secretary reported on the financial status of the Association and noted that operations for the first six months of 1956 were within the allocated budget.

Council discussed the matter of papers for annual meetings and the International Union of Leather Chemists Societies meeting. Upon motion by R. Weldon, seconded by E. D. Compton, it was unanimously agreed that full abstracts of papers submitted for either presentation at the annual meeting or at the International Union of Leather Chemists Societies meeting must be in the hands of the Convention Committee or the Awards Committee by January 1. A motion by R. Weldon, seconded by M. Maeser, and approved by Council, that all papers submitted for the prize award for attending the International Union of Leather Chemists Societies meeting must be submitted in complete form, to the Committee, by March 1; and papers for the annual meeting must be submitted in complete form to the Convention Chairman by May 1.

President Thorstensen agreed to appoint an Awards Committee and a Nominating Committee after considering the matters.

At the suggestion of Mr. O. Wederbrand, Council requested that President Thorstensen write a letter of explanation to each of the exhibitors, regarding the unsatisfactory exhibit space, to be sent out by Mr. Wederbrand.

In keeping with precedent, the Secretary-Treasurer and Chairman of the Ways and Means Committee submitted their resignations. The same were accepted, and both were reappointed for a new period of two years.

Council approved the recommendation that all technical committees remain as is until need of changes is shown.

Mr. Stanbery resigned from the Hide Powder Committee, and Mr. G. Daub will be asked to serve.

Mr. Weldon made a motion, and Council approved, that the Association should return to the Grand Hotel in 1959. Mr. Retzsch, chairman of the Convention Committee, will talk with the hotel staff about favorable dates in 1959.

It was suggested that a Transportation Committee be formed to serve as liaison with the transportation firms.

Messrs. Wederbrand and Retzsch will visit Lake Placid and review the location of the exhibits and report to Council at the next meeting.

The following associate members were elected to active status: T. Baltas, F. Brown, and L. Soesbe.

Mr. Wederbrand advised that the printing cost of the Journal had been increased 13%, and he recommended to Council that the advertising rates be increased about 15%. Council approved his recommendations.

The Editor-in-Chief and Managing Editor are to obtain bids from other printing firms on the cost of printing the Journal. Their recommendations will be considered at the October meeting.

The new Editorial Board, as selected by the Editor-in-Chief, was approved by Council. Members are:

E. D. Compton
J. H. Highberger
J. R. Kanagy
R. M. Koppenhoefer
W. T. Roddy
C. G. Telander
T. C. Thorstensen
H. G. Turley
R. H. Twining
C. D. Wilson

The next meeting of Council will be held in New York on October 18.

There being no further business, the meeting was adjourned at 10:25 A. M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary.*

In warfare and the realm of sport some form of mailed glove or gauntlet seems to have been in use from the earliest times of which we have any record. The "Cestus" or "Caestus" is mentioned in the account of the Trojan games, a thousand years before the Christian Era, in Virgil's Aeneid, Book V. They were used not only as weapons of offense, but also as tokens of defiance. They took several forms, but generally consisted of thongs of leather wound or plaited round the hands and weighted with metal. Some were particularly formidable, and a single blow from one was often sufficient to cause death.

—*Gloves and the Glove Trade*, B. Eldred Ellis. London: Sir Isaac Pitman & Sons Ltd., 1921

In the life of St. Columbanus, written by Jonas, Abbot of Bobbio (Italy), in the seventh century, gloves were spoken of as being used among the monks to protect the hands in manual labor. That they were in fairly general use among the French nobility is certain from the fact that the Emporor Charlemagne in A. D. 790 granted legal permission to the abbot and monks of Sithin for the hunting of deer in order that the skins might be available (among other things) for glovemaking.

—Ibid.

ABSTRACTS

Hydroxyproline and Stability of Collagen. K. H. Gustavson. *Acta Chem. Scand.*, **8,** 1298–99 (1954). (In English).—Proline (Pro) and hydroxyproline (Hypro) contents of collagen of calfskin, and of skins of pike and codfish, representing warm- and cold-water species respectively, were determined directly, employing a chromatographic technique. The results were as follows:

		Percentages of						
			Proline on		Hydroxypropline on		Pro + Hypro on	
Species	T_s °C.	Total N	Protein	Total N	Protein	Total N	Protein	Total N
Cod	40	18.3	10.8	7.2	5.8	3.4	16.6	10.6
Pike	55	18.4	13.3	8.8	7.9	4.6	21.2	13.4
Calf	65	18.3	14.1	9.5	12.7	7.4	26.8	16.9

Results confirm previously reported work in which Hypro was determined indirectly. The relationship between T_s and Hypro content supports the theory that the thermal stability of collagen is dependent in large measure on cross-links involving Hypro. Cross-linkage between hydroxyl groups of Hypro and side-chain carboxyls is shown to be improbable. **The Presence of Interchain Links Between Hydroxyl and Keto-imide Groups in Collagen.** *Ibid.*, 1299–1301.—About 3 out of 4 hydroxyls of Hypro residues in bovine collagen were blocked by O-acetylation. The T_s of the collagen (which is unaffected by N-acetylation), decreased by about 20°C. after O-acetylation. The O-acetylated collagen showed increased binding capacity for wattle tannin (bound chiefly at keto-imide groups), and decreased binding capacity for non-ionic Cr complexes (bound at various active centers including Hypro OH groups but not by keto-imide groups). These results support the hypothesis of H-bonding between OH of Hypro and CO of the keto-imide group. H.B.M.

The Functions of Hydroxylproline in Collagens. K. H. Gustavson. *Nature,* **175,** 70–74 (1956).—The data and conclusions are essentially the same as those previously published (see preceding abstract), but experimental procedures are given in greater detail, and the development of the hydroxyproline cross-link hypothesis is outlined. The "masked" hydroxyls (not susceptible to O-acetylation) probably form ester bonds. These may be the bonds that are common to all forms of collagen. 47 references. H.B.M.

The Isolation of Syringic Acid from Mimosa Tannin Extract. H. G. C. King. *Chem. and Ind.*, 658–59 (1956).—The ether: ethyl acetate fraction of commercial wattle extract was dissolved in water and extracted with ethyl acetate at pH 2. The extract was chromatographed and yielded 2 acids—gallic acid, and a second acid which was identified as syringic acid. The amount found was very minute. Syringic acid was found also in fresh wattle bark similarly fractionated and extracted. H.B.M.

A Study of the Photochemistry of Dyes on Proteins and Other Substrates. J. W. Cumming, C. H. Giles, and A. E. McEachran. *J. Soc. Dyers*

and Colourists, **72**, 373–81 (1956).—The fading of dyes in films of gelatin as a typical protein and methylethycellulose as a typical nonprotein has been studied. It is concluded that the photodegradation of a dye in a nonprotein film is oxidative, while in gelatin it is a reductive reaction. Histidine and possibly tryptophan side chains are suggested as the source of the reductant in the deterioration of the dye in the gelatin film. R.M.L.

Laboratory Estimation of Color Fastness. Publications Sponsored by the Society of Dyers and Colourists Fastnes Tests Co-ordinating Committee. *J. Soc. Dyers and Colourists*, **72**, 86–99, 330–32, 369–70, 431–33 (1956).—Spectral differences between the carbon arc light and sunlight seldom cause gross anomalies in light-fastness testing, but these spectral differences do render meaningless any attempts to equate a one-hour lamp exposure with so many hours of sunshine. Many of the discrepancies between daylight exposures and those made with fading lamps arise from differences in the effective humidity during exposure. The average humidity during daylight exposures in the United Kingdom is 20% and fading lamps should be operated at this humidity. Both temperature and humidity affect lamp fading response of several different dyes on wool. The final report covers some of the historical aspects of the selection of the graded series of blue standard for textiles. [Though this work is concerned solely with testing textile fading due to sunlight, unpublished studies on leather confirm the general aspects considered above, so that this report is recommended to those concerned with the fading of leathers.—*Abstracter.*] R.M.L.

The Influence of Histological Factors on the Attack of the Wool Fiber by Various Reagents. R. L. Elliott and J. B. Roberts. *J. Soc. Dyers and Colourists*, **72**. 370–73 (1956).—Significant variations in the stability of the histological components of the wool fiber to acidic and oxidative deteriorative agents have been noted. The lability of the orthocortex, the greater stability of the paracortex, and the existence of a stable subcuticular membrane is noted. In the degradation of wool fibers in boiling 2 *N* HCl, no free amino acids were found in 10 min.; aspartic acid, glutamic acid, serine, threonine, and proline were found in 20 min.; and all characteristic acids after 30 min. Except for proline, these acids are those previously found to be released readily from proteins. R.M.L.

The Photochemical Oxidation of Wool in the Presence of Fluorescent Compounds (Optical Bleaches). D. R. Graham and K. W. Statham. *J. Soc. Dyers and Colourists*, **72**, 434–38 (1956).—The oxidation of the amino acid tryptophan is the main reaction. R.M.L.

Spectrophotometric Studies on (Chrome) Metal-Dye Complexes. R. B. Bentley and J. P. Elder. *J. Soc. Dyers and Colourists*, **72**, 332–42 (1956). —Spectrophotometric and chromatographic studies have been applied to the complexes formed between the dye 2-hydroxy-5-sulfophenylazo-beta-naphthol (Solochrome Violet RS, C. I. No. 169) and chromic nitrate. Two intercon-

vertible complexes have been isolated chromatographically, and the equilibrium constants, heat, free energy, and entropy changes of the interconversion reaction determined. An excellent discussion is given of applicable physical chemical methods for study of chromium coordination complexes. R.M.L.

Extracellular Keratinase from a Streptomyces Species. J. J. Noval and W. J. Nickerson. *Bacteriol. Proc.*, 125–26 (1956).—A preliminary note. A strain of *Streptomyces*, grown in cultures with sterilized wool as the sole source of C and N, solublized 80% of the wool in 10 days. The cell-free filtrate from this culture solublized wool, hoof, or feathers in 5 hr. at 37°C. Soluble disulfide increased during digestion of wool, but no free –SH was detected, even when the digestion was carried out under N_2. The filtrates with keratolytic activity also digest casein. Optimum pH value for digestion of both wool and casein is 8.5–9.0. Wool digestion is stimulated by 0.001 *M* cyanide, and inhibited by 0.0001 *M* *p*-chloromercuribenzoate; neither of these affects casein digestion. The chelating agents, Na_2EDTA and 8-hydroxyquinoline (0.0001 *M*) inhibit both proteolytic activities. A longer paper is in preparation, and a patent application on the process has been filed. H.B.M.

Quantitative Determination of Amino Acids by Fluoresence of Derivatives on Paper. V. G. Shore and A. B. Pardee. *Anal. Chem.*, **28,** 1479 (1956).—This semiquantitative determination is effected by treating the chromatogram with a xylose spray, heating, and measuring the fluorescence of the spots. H.R.W.

Studies on the Shrinkage Phenomenon. I. Tanning with Aliphatic Sulfonyl Chlorides. Y. Nayudamma and T. S. Ranganathan. *Bull. Central Leather Research Inst., Madras*, **2,** 319–23 (1956).—Acetone-dehydrated pelt was tanned with an alkyl sulfonyl chloride (Immergan) (see Jurney, *JALCA*, **44,** 14 [1949]). Portions of the resulting leather were retanned with Cr sulfate, wattle extract, HCHO, fish oil, and a syntan (Basyntan F.C.). Similarly, leathers were tanned initially with each of these agents, and a portion of each leather was retanned with Immergan. Shrink temperatures were measured for all the leathers, with the following results:

Tanning Material	Shrinkage Temperature, °C.		
	Single Tannage	Pretanned with RSO_2Cl	Retanned with RSO_2Cl
Immergan (RSO_2Cl)	61	....	....
Chrome	132	123	103
Vegetable (wattle)	80	82	74
Fish oil	64	66	69
Formaldehyde	91	86	89
Syntan (Basyntan FC)	67	63	63

The low shrink temperature of aliphatic sulfonyl chloride leather indicates absence of cross-linking. Since either pretanning or retanning with RSO_2Cl

lowers the shrink temperature of chrome, HCHO, or syntan leather, the RSO_2Cl may interfere with cross-linking by these tanning agents. The fact that either pretanning or retanning with RSO_2Cl raises the shrinkage temperature of leather tanned with fish oil suggests that the effective tanning constituents of fish oil may be fixed by groups other than the NH_2 group with which RSO_2Cl supposedly combines. If this is true, then the effective tanning agents in fish oils may be peroxides that combine with COOH groups, rather than aldehydes. H.B.M.

The Splitting of Hydrolyzable Tannins and the Effect of This in Practice. E. Komarek. *Das Leder*, **7**, 148–54 (1956).—The present knowledge of the structure of hydrolyzable tannins is reviewed briefly. (See O. Th. Schmidt, *Angewandte Chemie*, **68**, No. 3 [1956]). The practical man is interested in the fact that the cleavage products of these tannins, if soluble, have an affinity for collagen but no tanning ability. Skin treated with gallic or chebulic acids resembles dried rawhide rather than leather. If all of the tannin were split into its simple components the analytical figures would change only in so far as these components had no affinity for collagen, e. g., the sugars would appear as nontannin. But if splitting did not proceed far enough to set free sugar, there would be no change in the analysis. Investigations of the tannin balance, etc., based on tannin analyses therefore are worthless. The following table shows the analyses of 2 extracts adulterated with a mixture of gallic acid and glucose. For myrobalans the mixture contained gallic acid and glucose in the ratio 68.4:23.5, and for chestnut in the ratio 74.7:16.4.

Extract	Tannin %	Nontannin %	Tan Value 24 hr.	Combining Value	pH
100% myrobalans	68.4	23.5	90.2	41.8	3.30
90% myrobalans: 10% mixture	68.4	23.3	89.0	41.8	3.30
80% myrobalans: 20% mixture	68.1	23.9	86.8	41.7	3.25
70% myrobalans: 30% mixture	67.8	24.3	81.0	41.3	3.25
100% chestnut wood	74.7	16.4	88.0	60.8	3.65
90% chestnut: 10% mixture	74.4	16.7	88.5	57.3	3.40
80% chestnut: 20% mixture	73.4	18.1	84.3	52.8	3.30
70% chestnut: 30% mixture	72.7	19.7	81.0	50.2	3.20

It is surprising that the tan and combining values give little indication of the addition. If one tans a piece of skin with a well defined tannin such as chebulinic acid and a comparable piece with its cleavage products, glucose, chebulic acid, and gallic acid, in the proportions 1:1:3, the first piece will be soft, full leather and the second a horny mass with a tendency to break. The causes of the splitting or cleavage are self-hydrolysis and enzyme activity. The first is of minor importance in the pH range found in practice. Enzyme cleavage can cause great damage with little outward evidence unless insoluble matter is formed, such as. for example, the deposit of ellagic acid from valonia extract. Most of the enzyme is produced by molds growing on the tan liquor. *Aspergillus niger* and *Penicillium glaucum* have long been known to split tannin, and a small amount of tannase can split a large amount of tannin. Appreciable amounts of tannase are formed only when the mold is grown on hydrolyzable

tannin. Insolubles in an extract can be dissolved and used for tanning, but an ellagic acid deposit or "bloom" cannot be redissolved. Such a deposit on leather may cause irregular dyeing. Ellagic acid may be tested for by suspending some of the bloom or rasped leather in acetone and adding a little sodium nitrite and a few drops of glacial acetic acid. The solution turns intense red if ellagic acid is present. If the leather is dipped in dilute soda solution the intensely yellow sodium salt of ellagic acid will form. Mold growth can be prevented by fungicides, but they also affect the total microbiological activity and may prevent the fermentation that is so necessary for the development of proper acidity. Suitable syntans will control molds without affecting fermentation. An extract mixture of 60 parts of chestnut, 20 parts of wattle, and 20 parts of valonia extract, left undisturbed for 4 weeks, developed a heavy mold growth on the surface and a heavy sludge. A solution of 70 parts of the preceding extract mixture and 15 parts each of Tanigan extra NR and KNS developed no mold under the same circumstances. I.D.C.

Physicochemical Studies on the Skin and Leather of Marine Animals. IX. Swelling of Shark Skin—1. T. Takahashi. *Bull. Japan. Soc. Sci. Fisheries*, **19**, 1203–18 (1954). **X. The Proteins in Shark Skin.** T. Takahashi and W. Yokoyama. *Ibid*, **20**, 411–20 (1954). **XI. The Action of Trypsin on Fish Skin Collagen.** T. Takahashi and M. Takei. *Ibid.*, 421–30 (1954). **XII. The Content of Hydroxyproline in the Collagen of Different Fish Skins.** T. Takahashi and W. Yokoyama. *Ibid.*, 525–29 (1954). **XIII. The Swelling of Shark Skin—2.** T. Takahashi. *Ibid*, 1110–17 (1955). **XIV. Degeneration of Vegetable-tanned Shark Leather Due to Hydrochloric Acid.** *Ibid.*, 1118–24 (1955); *Chem. Abstr.*, **50**, 11695*d*.

Shrinkage Temperature of Vegetable-tanned Leather. E. Sugano. *Repts. Gov. Chem. Ind. Research Inst., Tokyo*, **49**, 99–105 (1954); *Chem. Abstr.*, **50**, 11698*h*.

Physical and Chemical Characteristics of Some Indian Leathers. I. Chemical Standards for E. I. Leathers. B. M. Das and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras*, **2**, 324–28 (1956).—The authors analyzed 6 E.I. goat, 6 E.I. sheep, and 3 E.I. kip leathers, all of which were commercial products made by reputable tanners. Results are tabulated. From these results, the following chemical specifications are recommended (applicable to all 3 types): Hide substance, 41–48; fats, 11 (?); water solubles, 5.6–10; pH of water solubles, 3.5–4.0; ash, 0.9 (max.); glucose, 0.4 (max.); Epsom salt, 1.0 (max.); fixed tannin, 24–28, degree of tannage, 52–67; leather content (hide substance plus fixed tannin), 65%. H.B.M.

Proposed Official Methods for the Determination of the Acidity of Vegetable-Tanned Leather. D. Burton (Convener). *J. Soc. Leather Trades' Chemists*, **40**, 245 (1956).—Three methods are proposed for the determination of the acidity of vegetable-tanned leather. The procedures employed

in the Procter-Searle (*J. Intern. Soc. Leather Trades' Chemists*, **23,** 273 [1939]) method, the Innes method (*Ibid.*, **12,** 256 [1928]), and the Atkin-Thompson method (*Ibid.*, **13,** 300 [1929]) are given in detail. J.M.C.

Proposed Official Method for the Determination of the Neutralization Value (Buffer Capacity) of Vegetable-Tanned Leather. D. Burton (Convener). *J. Soc. Leather Trades' Chemists*, **40,** 248 (1956).—The method of Burton (*J. Intern. Soc. Leather Trades' Chemists*, **21,** 254 [1937]) is given in detail. J.M.C.

Proposed Official Methods for Analysis of Sulfated Oils. D. Burton, G. F. Robertshaw, and C. H. Pearson. *J. Soc. Leather Trades' Chemists*, **40,** 248 (1956).—The procedure is outlined in detail for sampling, examination, and determination of H_2O, pH, ash, acid value, unsaponifiables, total alkalinity, organically combined SO_3 existing as (1) neutralized sulfuric esters and (2) neutralized sulfonic acid groups, inorganic sulfate, and chloride. J.M.C.

Comparative Tests of the Effectiveness of DDT and BHC Dusting Powders Against the "Hide or Leather Beetle", Dermestes Maculatus Degeer (Col. Dermestidae). G. C. Williams. *J. Soc. Leather Trades' Chemists*, **40,** 253 (1956).—BHC (lindane quality) applied as a dusting powder produced a rapid extermination of *D. maculatus* adults. DDT was less effective. DDT is ineffective against *D. maculatus* larvae. The reaction of the BHC with larvae is slower than with adults but still effective. J.M.C.

A Survey of Skin Diseases of Goats in Kenya and Their Effect on the Finished Leather. H. F. Green. *J. Soc. Leather Trades' Chemists*, **40,** 259 (1956).—Approximately 8000 dried goat skins were examined. The diseases were grouped according to general appearance and characteristics of the skin lesions. A number of selected specimens from each group were used for laboratory identification. The effect of lesions on the skin structure was ascertained by histological examination. Effect on finished leather was determined by tanning selected specimens. The diseases are described and illustrated as they appear on the dry, raw skins. Demodicosis and streptothricosis were most prevalent and most damaging to the leather. A third prevalent disease, unidentified, and referred to as "scurf", had little adverse effect on the leather. J.M.C.

The Use of Hide Powder Analysis for Evaluating the Tannin Balance in Vegetable Tanning. P. J. van Vlimmeren. *J. Soc. Leather Trades' Chemists*, **40,** 265 (1956).—A method is proposed for drawing up a tannin balance in vegetable tanning. Pelt and chromed hide powder gave the same result, but for convenience the latter is preferred. In vegetable tanning a suitable balance can be obtained even with a tannin containing much semi-tannins by analyzing the leather in the usual way and the liquors by either

the filter-bell or shake methods; the latter is preferred since it is faster and internationally accepted. For used liquors containing excessive semi- and non-tannins, the analytical solution must be of the prescribed strength to avoid misleading results. The Nx5.62 factor for hide substance is apparently too high for tanned leather. Water of hydration (so-called bound water) of hide substance is displaced by vegetable tannins and the factor reduced to an extent depending on the intensity of the tannage. J.M.C.

Structure and Composition of Soluble Feather Keratin. A. M. Woodin. *Biochem. J.*, **63,** 576 (1956).—Keratin derivatives were obtained (1) by extracting with urea at 40°C., dialysing, and freeze-drying the gel formed, and (2) by oxidizing the urea-extracted derivative with performic acid and again dialysing and freeze-drying. Reactions with 1-fluoro-2:4-dinitrobenzene (FDNB) and with phenyl isothiocyanate indicated that the soluble keratin contained only 0.1 equivalent of N-terminal amino groups per mole of protein. Reaction with carboxypeptidase indicated absence of a molar proportion of α-carboxyl groups. Quantitative data is given for the amino acids of keratin extracted with urea and oxidized with performic acid. Conclusion: the feather keratin monomer (mol. wt. 10,000) is an unbranched cyclic polypeptide. J.M.C.

Differentiation of Some Natural Tannin Extracts by Paper Chromatographic Technique. L. W. Haddaway. *Anal. Chem.*, **28,** 1624 (1956).—A technique for the identification of a number of natural tannin extracts is based upon the selective adsorption, on plain blotter squares, of various components of the tannins from a mixed solvent composed of ethyl ether, butyl alcohol, and acetone. The resulting dried chromatogram is examined under the ultraviolet lamp. The method is empirical, yet the distinctive colored zones produced are adequate for the characterization of many tannin extracts. A table of the expected color zones is given to be used as a reference in the absence of, or to supplement, authentic samples. Author's Abstract

The Structure of Collagen—Observations and Models. P. M. Cowan, A. C. T. North, S. McGavin, R. E. Burge, S. Fitton-Jackson, and J. T. Randall. *Proc. 3rd Intern. Congr. Biochem. Brussels,* **1955,** 122–24 (in English); *Chem. Abstr.*, **50,** 12145*a*.

Collagen. I. Structure of the Collagen Group of Proteins. G. N. Ramachandran and G. Kartha. *Proc. Indian Acad. Sci.*, **42A,** 215–34 (1955); *Chem. Abstr.*, **50,** 12151*h*.

Manufacture of Chrome Tanning Agents by Electrolytic Reduction. II. Reduction of Chromate Compounds in Sulfamic Acid Solutions and the Tanning Properties of the Reduced Solution. T. Komuro and T. Uchida. *Repts. Govt. Chem. Ind. Research Inst., Tokyo,* **51,** 199–205 (1956); *Chem. Abstr.*, **50,** 12617*i*.

Train Oil Oxidation Products Formed under the Conditions of Chamois Tanning. I. The Formation of Polymerization Products and Alteration of their Constants During Autoxidation of Chamois Tanners' Train Oils. A. Küntzel and Th. Nungesser. *Das Leder*, **7**, 73–78 (1956). —In an earlier study (abstracted *JALCA*, **47**, 205 [1952]) of the autoxidation of chamois tanning oils, the Mackay apparatus was used to obtain time-temperature curves to show rate of oxidation, and acrolein was found in the volatile material formed during oxidation. In the present work, the rate was not studied, but volatile and insoluble products were determined. The reaction chamber was a 160×33 mm. glass tube immersed in a water bath at 80°C. During a test 7–7.5 l. per hr. of air (heated by passing through a copper coil in the bath) was pulled through the chamber. The oil sample, dissolved in ether, was applied to a fat-extracted, weighed cotton wad by saturating the wad with the solution, squeezing, drying in a stream of N_2, and reweighing. A 6-g. wad took up from 6 to 9 g. of oil. The wad was placed in an aluminum wire cage so no oil was lost on the walls of the chamber. During oxidation, volatile products (except CO_2) were collected in a solution of 2,4-dinitrophenyl hydrazine, and CO_2 was collected in a soda lime tube. After a 5-hr. oxidation period, the wad was extracted with CCl_4 for several hours in a Soxhlet extractor to determine insoluble matter. The constants of the extracted, oxidized oil were determined and compared with those of the original oil. Preliminary tests showed that the greater the surface area of the cotton, the greater the amount of decomposition products, but that a tightly packed wad resulted in more volatiles. The oils were analyzed by standard methods. Iodine numbers were determined by the Kaufmann method, which gave constant values, whereas the Hanus method did not. Tables show analyses of the oils before and after oxidation. The oils were light and dark cod, light seal, herring and shark oils, and free fatty acids of these oils (except herring). Autoxidation increased the acid number because of hydrolysis of triglycerides and also formation of new acids. Saponification number increased both because of esterification of newly formed acids and alcohols and also because unsaturated fatty acids decomposed into triglycerides of fatty acids with shorter chains. The difference between the iodine number and the thiocyanogen number (discrepance) decreased, indicating a decrease in polyunsaturated acids. The diene number decreased somewhat; conjugated fatty acids, if formed, reacted further at once. The hydroxyl values and carbonyl numbers were not high, because newly formed alcohols disappeared at once through esterification, and carbonyl compounds were in general volatile. The marked changes were the rise in saponification number and the decrease in iodine number. Although there was a loss of volatile material, mainly carbonyls, yet the oil on the wad increased in weight by 3–6%. The greatest yield of hydrazone was 6–7% (oil basis), corresponding to 1.4–1.8% of acrolein, from cod oil. The order of decreasing yield of hydrazone was: seal oil fatty acid, herring oil, seal oil, shark oil, shark oil fatty acid. This is approximately the order of tanning value assigned to them by the tanner. The unsaponifiables of shark oil produced 4.27% of hydrazone, showing that squalene takes part in chamois tanning. In all the oxidations, between 1 and 3.5% (oil basis) of carbon dioxide was formed, and the presence of carbon monoxide was shown by qualitative tests with $PdCl_2$. The brown insoluble matter remaining on the cotton wad after extraction with organic solvents amounted to 10–20% of the original oil for cod and seal oil fatty acids. This explains why chamois tanning with free fatty acids produces

hard rather than soft, flexible leather. Polymerization products of fatty acids are detrimental to leather properties because of their amount and their compact structure. Polymers of triglycerides have a more open network structure and coat the fibers with a finer, softer film than do the polymers of the isolated fatty acids. The order of tendency of oils to form insoluble polymers is: light cod, seal, dark cod, and herring. Shark oil made chamois leather that was empty and tinny, although satisfactory in other respects; it also produced no insolubles, showing that coating of the individual leather fibers with an oil polymer film is an important factor in tanning. The polymerization product is identical with the so-called bound fat, although tanning aldehydes probably have a share in the analytically determined "bound fat". The argument that the polymer does not coat the fibers but is united to hydroxyl groups of the cotton is disproved by the facts that (1) shark oil behavior is different from that of cod and seal oils, and (2) results with asbestos were the same as those with cotton. Paper chromatographic separations of the oxidized oils were made by the method of Kaufmann *et.al.* (*Fette und Seifen*, **54**, 348 [1952]). Polymers, which remained at the starting point on the chromatogram, were not found in the original oils but were present in all oxidized oils except shark. In practice, a temperature of 80°C. is seldom reached, therefore an autoxication was conducted at room temperature for 200 hours. Polymers and volatile products were found as before, indicating that the results at 80°C. were not exceptional. Analysis of a commercial degras showed that in chamois tanning there are oxidative changes corresponding closely to those found in the laboratory experiments.

II. Paper Chromatographic Separation of the 2,4-Dinitrophenyl Hydrazones of Volatile Train Oil Oxidation Products. *Ibid*, **7**, 115–19 (1956).—Methods for the separation of dinitrophenyl hydrazones of aldehydes and ketones are reviewed. Only chromatographic methods can be used. The method of Neiman, Lewkowsky and Lukownikow (*Ber. Akad. Wiss. UdSSR*, **81**, 841 [1951]) was found to be satisfactory when their method for acetylation of the paper was modified to give a less fragile paper. A rising column chromatogram was prepared by applying a few cubic millimeters of a 1% solution of the hydrazone in tetrahydrofurane or ethyl acetate to the acetylated paper and developing at 40°C. with 96% ethyl alcohol. Development with water-immiscible solvents or water-miscible solvents containing too much water gave very poor results. Visibility of the spots was improved by spraying with a 10% solution of KOH. R_f values were not satisfactory for identifying the spots because of variations in degree of acetylation of the paper. Direct comparisons were made with dinitrophenyl hydrazones of known aldehydes and ketones (formaldehyde, acetaldehyde, propionaldehyde, acrolein, crotonaldehyde, glyoxal, pyruvic acid, and diacetal). These standards had R_f values of 0.3-0.7, except the glyoxal hydrazone. The spots for the hydrazones of formaldehyde, acetaldehyde, propionaldehyde, and acrolein were well separated, but hydrazones of acetaldehyde, acrolein, and crotonaldehyde in a mixture could not be distinguished. Chromatograms are shown of dinitrophenyl hydrazones of the volatile material from oxidized cod, herring, and shark oils. Part of the oil derivative remained at the starting point; these spots when sprayed with KOH solution turned blue (or in some cases violet, greenish, or brownish) indicating the presence of a dialdehyde hydrazone. No spots from any of the train oils formed a carmine red color when sprayed with KOH; this is evidence for the absence of ketones. There was no essential difference between chromatograms for an oil and the

free fatty acids from the oil. For oils oxidized at 80°C., spots were found corresponding to higher aldehydes such as hexanal or heptanal. These spots were not found if the oil was oxidized at 20°C., probably because these aldehydes were not volatile at 20°. There was no other difference between the chromatograms of dinitrophenyl hydrazones of volatile products from oils oxidized at 20° and 80° C. respectively. I.D.C.

The Reaction of Wool Keratin with Alkali. S. Blackburn and G. R. Lee. *Biochem. et Biophys. Acta*, **19,** 505–12 (1956).—Lanthionine and cystine were determined in acid hydrolyzates of virgin wool and wools treated at the boiling point with buffers (pH 7 to 10) or with 1% Na_2CO_3; in the last case only 18% of the wool remained undissolved. Lanthionine was determined by the authors' method (*Chem. and Ind.*, **1954,** 1252) and cystine by Shinohara's method and by oxidation to cysteic acid with HCOOH–H_2O_2; the former method gave higher results. In no case did the sum of lanthionine, cystine, Br-oxidizable S, and methionine in the hydrolyzate equal to total S. Virgin wool contained practically no lanthionine (0.01%). The percentage of lanthionine increased, and that of cystine decreased, with increasing severity of the alkaline treatment, but the residue from the treatment with boiling 1% Na_2CO_3 still contained 0.35% cystine S. While cystine linkages in keratin vary in their resistance to alkali, the authors believe that there is no sharp division into fractions reacting with alkali by different mechanisms. Differences in reactivity of cystine groups probably are caused by the effects of adjacent amino acid residues. For each 2 atoms of cystine sulfur lost by the keratin, one lanthionine molecule is formed. This indicates that the reaction is almost entirely the conversion of cystine to lanthionine, and that the alternative postulated reaction, whereby a cystine group yields 2 molecules of α-amino acrylic acid, with loss of 2 sulfur atoms, does not take place to any appreciable extent. The pyruvic acid in the hydrolyzate, supposed to be evidence for the latter reaction, probably is derived from α-amino acrylic acid formed by alkaline decomposition of serine rather than cystine. Complete amino-acid analyses were made by Moore and Stein's method on acid hydrolyzates of virgin wool and wool boiled with a buffer at pH 10. The weights of cystine, serine, and threonine obtained from 100 g. wool decreased by about 67, 20, and 10% respectively as the result of the alkaline treatment. Changes for all other amino acids are regarded as nonsignificant. H.B.M.

The Hydrolysis of the Chromium Sulfates. J. I. Aznarez and J. V. Vinade. *Anales real soc. espan. fis. e quim.*, **52B,** 331–38 (1956); *Chem. Abstr.* **50,** 12719*h*.

Separation of Ferric Iron from Chrome by Ion Exchange Resin. G. Venturello and C. Gualandi. *Ann. chim.* (Rome) **46,** 229–34 (1956); *Chem. Abstr.*, **50,** 12739*a*.

Analysis of Complex Chromium Ions with Ion Exchange Resins. III. Exchange Reactions between Polystyrene-Type Cationic Exchanger and Cationic Chromium Complex Ions. Y. Inoue, A. Kawamura, K. Wada, and H. Okamura. *Japan Analyst*, **4,** 277–80 (1955). **IV. Analyses of Complex Chromium Ions with Polystyrenesulfonic Acid and Amberlite** IR-4B. *Ibid.*, 281–85 (1955); *Chem. Abstr.*, **50,** 12751*b*.

BOOK REVIEWS

Reports and Papers—The Research Laboratory of the Tanners' Council of America, Inc., 1949–1955. Volume VII. New York: Tanners' Council of America, 411 Fifth Ave. $5.00.

Volumes I to VI of this series appeared in 1951 and comprised the collected publications of the Tanners' Council Research Laboratory from 1924 to 1949. Volume VII completes the collection through December, 1954. The cost of publication has been borne by the Foundation of the Tanners' Research Laboratory, and the not inconsiderable labor of indexing and preparing the book for the press was done by the Laboratory staff. All concerned deserve the thanks of the leather industry for making this collection available. While a large majority of the 72 papers appeared originally in this Journal, a considerable number were published in the various trade magazines. The preservation of these latter contributions is one of the many useful functions that this work has accomplished.

The reviewer would suggest that, when it is time to assemble Volume VIII, consideration be given to arranging the papers by topics, instead of in chronological order. At least this should be done for each group of papers comprising a series. H.B.M.

Handbook of Chemistry and Physics. 9th ed. Compiled and edited by Norbert A. Lange and Gordon M. Foster. Sandusky, Ohio. Handbook Publishers, Inc., 1956. xvi + 1969 pp. $8.50.

This well known and widely used handbook needs no lengthy review. This is the ninth edition to appear in 22 years, which is sufficient evidence of the continued popularity of the book and of the determination of its editors and publishers to keep it up-to-date. This edition contains 19 wholly new sections, some of which, to be sure, such as Cosmic Abundance of Chemical Elements, have no immediate bearing on the manufacture of leather. Many others will be of value to chemists and chemical engineers in the leather industry. Among these are: Properties of Plastics, Steels, and Non-Ferrous Alloys; Polarography; Activity Coefficients of Ions; Drying Agents; Relative Humidities and Aqueous Tensions of Sulfuric Acid, Sodium Hydroxide, and Calcium Chloride Solutions; Viscosity Comparison Charts; and Hydrometer Scale Comparisons. Tables that have been rewritten completely for this edition include: Corrosion and Heat-resistant Alloys; Calibration Tables for Thermocouples; Electrometric Determination of pH [excellent]; Organic Reagents for Analysis; Densities and Specific Gravities of Aqueous Solutions; Solutions for Maintaining Constant Humidity; and Viscosity Conversion Tables. Numerous revised values for the properties of elements, compounds, and commercial materials have been incorporated in the appropriate tables.

A good, comprehensive handbook is as much a laboratory necessity as a balance, a sink, and an ash tray. This is a good one, and cheap at the price. The typography, paper, and binding are up to the high standard established by previous editions. H.B.M.

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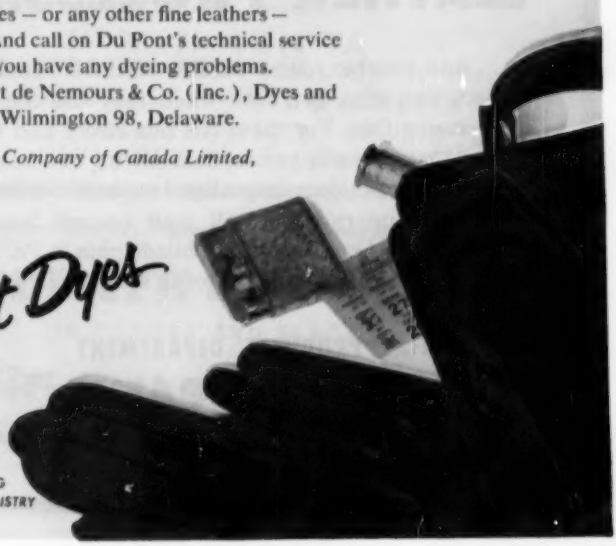

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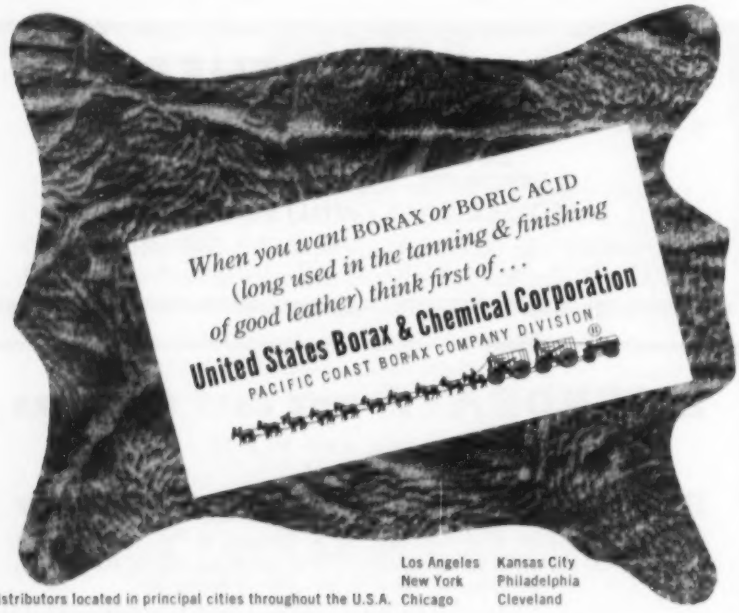
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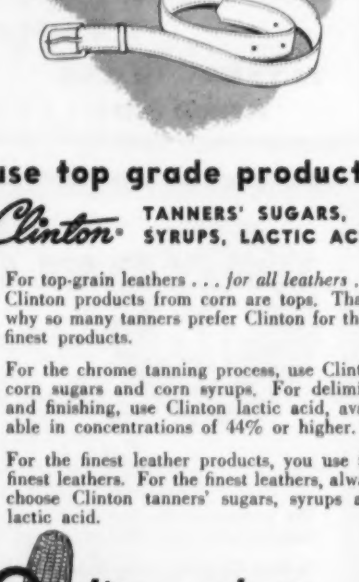
when tanning top-grain leathers . . .



use top grade products

Clinton® TANNERS' SUGARS, SYRUPS, LACTIC ACID

For top-grain leathers . . . *for all leathers* . . . Clinton products from corn are tops. That's why so many tanners prefer Clinton for their finest products.

For the chrome tanning process, use Clinton corn sugars and corn syrups. For deliming and finishing, use Clinton lactic acid, available in concentrations of 44% or higher.

For the finest leather products, you use the finest leathers. For the finest leathers, always choose Clinton tanners' sugars, syrups and lactic acid.

Quality products

FROM THE WORLD'S CORN CENTER

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MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN	16.03	17.14
INSOLUBLES	1.70	0.72
WATER	20.72	17.80

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

TANEXCO, INC.

549 WEST WASHINGTON BLVD., CHICAGO 6, ILLINOIS

SOLE DISTRIBUTORS OF THE TRADE

U. S. A.

Mutual's name for their basic chromic sulfate used in one-bath chrome tanning. Available in two grades with approximate analyses as shown below.

	Koreon M	Koreon X
Cr_2O_3	24%	25%
Basicity (Schorlemmer)	33%	52%

Koreon is packed in multi-wall paper bags containing 75 pounds, and in fibre drums containing about 325 pounds.

SODIUM BICHROMATE POTASSIUM BICHROMATE

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MUTUAL — ALLIED CHEMICAL & DYE CORPORATION

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